INDUSTRIAL HYGIENE CHARACTERIZATION
OF THE
PHOTOVOLTAIC SOLAR CELL INDUSTRY

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ABSTRACT

The search for viable alternative energy sources has intensified interest in photovoltaic technologies. Although this industry is currently very small, rapid growth is anticipated during the remainder of this century. This expected growth in the production of photovoltaic devices and related base materials and its attendant increased work force warrant an evaluation of the potential occupational health and safety hazards of the industry.

The information presented in this report is based on a comprehensive literature review and walk-through surveys of 14 production or research and development facilities. The investigation covers the technology from base material preparation through final module assembly. Descriptions are given of major technologies under development and the associated chemical and physical agents to which workers could be exposed.

In-depth sampling surveys were conducted. Industrial hygiene concerns connected with each major technology are presented. Available health effects literature is listed for the chemicals used in all reviewed technologies.

The investigation revealed that of the facilities surveyed, the industry presently appears to be generally well controlled, especially as to the single crystal silicon technology which is the most highly developed technology in the industry. Comprehensive industrial hygiene sampling was performed in a few facilities regarded as representing the norm. With the exception of elevated exposures to silver during grid metalization in one facility and to arsenic during gallium arsenide wafer production in another facility, all other exposures monitored were well within the standards. It must be realized, however, that toxic compounds are used and continued surveillance within the industry during its growth should be maintained.

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1. SUMMARY

This report deals with a study of industrial hygiene concerns in the photovoltaics industry, with emphasis on solar energy applications. The purpose of the report is to identify potential occupational problems in this growing industry so that action can be taken before chronic, long-term health effects develop. The report is based on information from the literature and from a survey of 14 of the major plants in the industry. The survey consisted of walk-through tours of plant facilities; at some of the plants, in-depth sampling was performed with personal monitors and area samplers. The study was sponsored by the National Institute for Occupational Safety and Health (NIOSH) and conducted by PEDCo Environmental, Inc., in collaboration with Occusafe, Inc.

Assessment of industrial hygiene problems that confront the industry entails a review of the technology of photovoltaic cell production and the toxicology of the materials used. Therefore, the report presents a relatively current discussion of the major cell production technologies in photovoltaics: Single-crystal silicon solar cells, cadmium sulfide solar cells, gallium arsenide solar cells, and amorphous silicon solar cells. Emphasis is on single-crystal silicon solar cells because they have been researched far more than any other solar cell and they are the only ones produced commercially. The technology for producing single-crystal silicon cells has been proven for the most part and will probably be used in the first large-scale production facility.

The review considers production of raw materials where such production has a significant impact on industrial hygiene aspects of the photovoltaics industry. It also considers commerical- and utility-scale photovoltaic installation systems and the hazards these systems might pose.

The study indicates that industrial hygiene practices are presently generally good throughout the photovoltaics industry. Because efforts to reduce costs have led to processes that minimize waste of materials, such efforts also minimize the exposure of workers. Ventilation controls were adequate in most cases; additionally, in the approach to many problems specific to the photovoltaics industry, worker health and safety are a primary concern. Technological changes and production growth should not adversely affect employees if proper concern is given to controlling exposures. Overall, the major potential industrial hygiene problems relate to accidental release of toxic materials and maintenance in areas where such materials are handled.

One health concern that must be given in-depth review is the carcinogenic status of arsenic and the suspect carcinogen status of cadmium. As carcinogens, the issue of threshold versus no threshold effect must be dealt with because the no threshold response presents containment problems. It appears that arsenic in gallium arsenide (GaAs) processes may not be adequately controlled.

The engineering control of cadmium in the CdS back-surface spray operation would have to be improved if cadmium were treated as a carcinogen. If these materials are recognized as carcinogens, the additional controls and health surveillance programs required would increase the cost of these processes and could significantly affect the attractiveness of some of the technologies. This important issue should be resolved while the industry is in an early developmental stage. Other materials such as selenium and beryllium, which also are suspect carcinogens used in this industry, should be evaluated in a similar manner.

It is emphasized that the photovoltaics industry is in its infancy. Single-crystal silicon cells are the only ones being produced commercially, and some processes that are important in terms of industrial safety and hygiene may be less widely used in the near future. Future process designs will likely be more highly automated, less wasteful of materials, and better controlled. Contact of workers with materials should be minimal in most processes.

Current processes for porduction of cadmium sulfide cells are on a pilot scale. Again, with the development of full-scale production, many operations now requiring operator intervention at the pilot-scale level will be automated.

Production of gallium arsenide and amorphous silicon cells is in developmental stages, and not yet amenable to comprehensive industrial hygiene assessment. Because the industry is young, technological improvement is needed in many areas. The following is a summary of observations and recommendations concerning health and safety in the major segments of the industry.

This study should be repeated in 5 years to incorporate new technology and to evaluate the status of industrial hygiene control. By that time the photovoltaics production level should be much higher and the number competitive technologies should be fewer.

SINGLE-CRYSTAL SILICON CELLS

Production of metallurgical-grade silicon will involve a certain amount of exposure to crystalline silica; however, the nature and extent of the exposure are yet to be determined. More data are also needed on exposure levels and potential health effects of metallic silicon, because workers may be exposed during the milling of metallurgical-grade silicon. Production of polycrystalline silicon generates several chlorosilanes; the toxicity data are sparse and more are needed. It would be advisable to design engineering controls to handle the worst case HCl concentration in the event of an accidental release of chlorosilanes. Monitors with alarms should also be provided in the polysilicon production area to detect any hydrogen buildup.

The alternative processes for polysilicon production also introduce some compounds for which additional toxicological data are needed to determine potential acute and chronic effects. These substances include silane, silicon tetrafluoride, fluosilicic acid, silicon sodium fluoride, cryolite, and silicon difluoride. The proposed Westinghouse and SRI processes use metallic sodium. Special precautions should be taken to ensure safe storage, handling, and transport of the sodium, because its high reactivity creates a potentially serious hazard.

The Czochralski single-crystal growth process, used predominantly throughout the industry, is a proven and relatively safe technology. New single-crystal growth technologies also appear to present few hazards. If the laser zone crystallization process becomes widely used, shielding will be needed to protect workers from laser hazards. Lasers may also be used eventually in slicing single-crystal ignots and in annealing.

Wet chemical etching and cleaning processes predominate in the industry. Acids, bases, solvents, and oxidants used in these processes can pose a threat to worker health and safety. The health effects of most acids and bases are well known, but little information is available on many solvents and oxidants. Because some of these materials are sensitizing agents, skin contact must be avoided. Uniform ventilation is required over liquid baths, with fail-safe systems in case of ventilation failure. These controls are proven technology. It is desirable to minimize the liquid surface area exposed to the atmosphere by covering the tanks. Automation of these operations is also suggested.

Plasma etching and cleaning is likely to be used increasingly. Emissions from this process can be controlled with adequate ventilation. Carbon tetrafluoride is often used as the plasma gas. Additional toxicological information is needed on this compound and others that may be formed in this process.

In junction formation or doping, several toxic gases are used, including phosphine, arsine, and diborane. It is essential that cylinders containing dopant gases be stored within well-ventilated enclosures. Ventilation systems should be equipped with fail-safe alarm systems and with emergency exhaust in the event of system failure. Ion implantation, which is expected to be used increasingly for junction formation, should present few problems because it is an enclosed vacuum process that can be controlled. Automation should effectively reduce worker exposure even further.

A number of processes take place under vacuum. It is important that vacuum pumps are designed with materials that are resistant to the gases, liquids, and solids that might be encountered. Many of the substances are abrasive and corrosive and could cause pumps to leak. Vacuum pumps should incorporate a fail-safe design. Pump maintenance and repair is a potential source of worker exposure. Routine maintenance and use of long-lived pump oils that are resistant to breakdown can reduce pump downtime and extensive maintenance.

The precautions discussed above apply also to vacuum metallization. In printing metallization, adequate ventilation is needed to remove the solvent and possibly some metal fumes when the cell is printed and fired or dried. As with etching, uniform ventilation is required for plating baths when electroless plating metallization is used. Because these solutions may contain concentrated metals and acids, the process should be automated as much as possible to minimize operator exposures.

Although the toxicity of antireflective coatings appears to be low, the exact compositions of all spin-on, spray-on, or paint-on coatings have not been determined. Where these coatings are used, the ventilation systems should be designed with flow rates based on the potential hazard of coating components. Where the antireflective coatings are vacuum-applied, the guidelines discussed above for vacuum processes should be followed. Application of a silicon nitride coating by chemical vapor deposition probably can be effectively controlled; more toxicological information is needed on this compound, however.

Module assembly will likely be the most labor-intensive process in a photovoltaic plant. Soldering and welding operations must be well ventilated by adequate methods, although as these operations become automated, worker presence will be minimal. Adhesives may be used in module assembly, and solvents in cleaning of the finished modules. Adequate ventilation and proper personal hygiene will be important in controlling exposures.

Additional information is needed on the chronic health effects of crystalline silicon, which is present in airborne particulate emissions from many of the processing operations.

CADMIUM SULFIDE CELLS

In the back-surface spray process all operations involving application or removal of cadmium (e.g., grid line scraping) should be isolated to prevent contamination of other plant areas. Ventilation should be designed so that ductwork for each operation is isolated and so that all systems draw contaminated air away from workers. In the arc operation for removing tin, workers should wear eye protection devices, and shielding should be provided to protect against exposure to ultraviolet light. Additionally, precautions should be taken to prevent exposure of workers mixing cadmium sulfide spray solution.

Adequate housekeeping practices can prevent buildup of cadmium on surfaces and thus protect workers from accidental contamination. Maintenance and repair of equipment is a major source of potential exposure. Results of a sampling survey of a process with cadmium sulfide back-surface spray technology indicated that maximum worker exposures occurred during cleanup operations. Appropriate design changes and engineering controls are needed to eliminate worker involvement in this operation. Because the plant surveyed is a pilot-scale facility, many design features that could be incorporated into a full-scale operation to reduce maintenance were absent. The potential for significant reduction of maintenance in a full-scale facility also should greatly reduce the exposure potential.

Additional toxicological information is needed on thiourea and N,N,dimethylthiourea and also on semiconductor materials being investigated, including indium and indium phosphide, copper indium selenide, and various other I-III-VI (valence) compounds.

In the front-surface process where the cadmium sulfide is vacuum-applied, designers must consider control of the exhaust gas and maintenance procedures for the vacuum chamber and the vacuum pump. Other processing steps appear similar to these in single-crystal silicon technology.

GALLIUM ARSENIDE CELLS

The major concern in the manufacture of gallium arsenide cells is potential exposure to arsenic. Although the zone tube furnace process for producing polycrystalline GaAs is enclosed and is under vacuum, any system failure could result in release of arsenic or arsenic trioxide. The ventilation design should incorporate a backup system and fail-safe alarm systems. Vacuum pumps should be of high quality to prevent leakage or failure. Stringent maintenance procedures are needed to minimize pump failures.

The single-crystal pulling process takes place in a pressurized atmosphere of close to 100 atmospheres. A failure within the system, such as a crack in the crucible, could cause the release of significant quantities of arsenic. It is important that the pullers have an emergency ventilation system equipped with a monitor to prevent contamination of other areas in the event of an accidental release. Small amounts of arsenic trioxide may be released during normal operations; adequate housekeeping is therefore needed to prevent inadvertent contamination of other areas. The liquid-phase and vapor-phase epitaxial growth processes should be equipped with sophisticated ventilation systems to prevent the release into the workplace or atmosphere of such contaminants as arsenic, arsine, gallium arsenide, and the organo-metallic gases such as trimethylgallium, trimethylaluminum, and diethyl zinc. Toxicological information on gallium, gallium arsenide, and the organo-metallic gases is scarce, and more is needed. In one plant exhaust gases are essentially hydrogen which is stored on the premises. An automatic hydrogen detection system equipped with automatic alarm is used in this area, and such systems are recommended for similar facilities.

Because gallium arsenide technology is many years from commercialization, a detailed industrial hygiene evaluation is not yet possible.

AMORPHOUS SILICON CELLS

Industrial hygiene concerns at this time appear minimal. Since most work on amorphous silicon cells is being done on a laboratory scale. Very small amounts of materials are used, and these are carefully controlled to prevent waste. Most processes take place in enclosed vacuum chambers. Exhaust ventilation must be designed to handle silane and diborane, which combust spontaneously. Control can be achieved by exhausting these gases with argon or another inert gas. A more detailed industrial hygiene assessment will be possible when pilot-scale facilities are in operation.

PHOTOVOLTAIC UTILITY INSTALLATIONS

Primary health concerns regarding the use of photovoltaic devices for power generation at a central utility are safety, electrical shock, and burns, the latter related only to concentrator units. Design of the utility installations must provide protection against these hazards.

2. INTRODUCTION

The need for alternative energy sources has brought about an increased interest in solar energy, in both the thermal and photovoltaic technologies. The anticipated increase in photovoltaic cell applications has prompted research into more rapid and less costly means of production so that this energy source can compete with others now in use and under development. This anticipated increase in production will most likely necessitate an increase in workers for photovoltaic cell manufacture. Because production of photovoltaic cells has been done on a small scale, the numbers of workers involved are accordingly small. The expected increases in output and in the number of workers warrant an evaluation of the potential occupational safety and health hazards of this industry.

Because the industry is in its infancy, little information is available concerning actual occupational hazards. Therefore, where it is available, information on currently operating industries (primarily the semiconductor industry) that involve similar practices and materials is extrapolated to apply to photovoltaic cell production.

Photovoltaic energy systems provide a method for direct conversion of sunlight to electrical energy. When light energy strikes a semiconductor surface on a photovoltaic device, an internal voltage is created. With suitable design, arrays of photovoltaic cells can be interconnected to provide specified levels of voltage and current. These systems are designed in modular form and thus are suitable for a wide range of applications.

Currently the photovoltaics industry is very small, the major product uses being in space applications or in specialized terrestrial applications such as power generation at remote weather stations. Commercial sales have been limited to small, remote markets, primarily communications and cathodic protection (1). Domestic production in 1978 was only about 0.5 MW/ year; projections for 1986 production, however, indicate growth to 250 MW/year. It is anticipated that by 1990 photovoltaic systems will be cost-effective for utility applications (2). Major potential markets include residential and commercial, as well as utility applications. Thus, this industry is being studied as an emerging potentially major energy technology.

The surge in research and development is due primarily to heavy government funding in an effort to reduce development time and focus on the most attractive alternatives. The primary goal is to produce a solar cell with a life expectancy of at least 20 years, a conversion efficiency of at least 10 percent, and a cost at least as low as $0.50 per peak watt (Wp). It it hoped that these goals can be accomplished by 1986, and that by 1990 the cell costs can be reduced to $0.10 to $0.30 per Wp (2).

The current national photovoltaic program is attempting to reduce current high prices of photovoltaics through three parallel approaches (1). The first approach is development of new photovoltaic technologies such as thin-film solar cells. Second is the continued development of current photovoltaic technologies, such as flat-plate and concentrator single-crystal silicon cells through improvements in array design and production techniques. Third is a market strategy aimed at stimulating markets and investment by the private sector in cost-reducing production facilities.

Currently, most attention in large-scale production is focused on silicon cell systems. The Low-Cost Solar Array project, (LSA) cosponsored by the Department of Energy (DOE) and NASA's Jet Propulsion Laboratory (JPL), is focusing on the second approach mentioned above. Because there is a 3- to 5-year span between technological and industrial readiness, the LSA objective is to develop the technologies for silicon cell production by 1981, 5 years ahead of the 1986 production goal (3). In an effort to realize the cost goal of $500/kW factory ($0.50/Wp) by 1986, the project is concentrated in the following areas (3):

> Development of low-cost polycrystalline silicon (polysilicon) production processes.
>
> Development of cheaper alternatives to single-crystal silicon growth processes.
>
> Development and scaleup of low-cost cell fabrication processes compatible with the two processes above.
>
> Development of low-cost module fabrication processes compatible with all the technologies above.

These areas are discussed in more detail later.

Though silicon-based systems are receiving the most attention, systems using thin films of CdS/Cu_2S are also well advanced in the developmental stages. Most work with CdS/Cu_2S has been accomplished by private industry. A number of other systems, most notably gallium arsenide (GaAs)(both single-crystal concentrator and thin-film polycrystalline cells) are also well into developmental stages. Great strides have been made in the development of thin-film amorphous silicon cells, which appear to be a promising alternative.

The ultimate goal in development of photovoltaic systems is to help relieve our dependence on oil, gas, and coal by increasing the use of these systems in residential, industrial, and utility applications. If this goal is to be realized in the next 10 years, the increase in production of photovoltaic systems must be phenomenal.

The National Institute for Occupational Safety and Health (NIOSH) is currently conducting health research studies of various developing energy technologies. It is anticipated that production of photovoltaic cells and systems will become a significant industry in the near future; thus it is important to assess the potential health and safety risks that workers may encounter.

This review provides descriptions of the current manufacturing technologies and the related potential worker health and safety hazards. Where it is possible, the developing technologies are described. Because the advances in photovoltaics are rapid, however, keeping pace with all of the new developments is beyond the scope of this report. Major emphasis therefore is placed on established technologies and on the newer ones that show promise for widespread use. The report focuses on silicon cell technology but also includes technologies for cadmium sulfide, gallium arsenide, and amorphous silicon systems. Other types of solar cells are discussed briefly. A review of the literature on photovoltaic installations is also presented.

The input for this report is primarily information obtained from the literature and from PEDCo and Occusafe surveys of 14 plants producing solar cells or materials used in solar cell production. In an effort to protect the proprietary aspects of information concerning the various plants, those plants are designated throughout the report as Plants A through N. An alphabetical listing of plants visited is presented in an appendix, as are detailed reports of the plant surveys.

The scope of this review includes raw materials production to the extent that this phase of the industry presents a significant impact on photovoltaics production and installation. The starting point for silicon cell production is production of metallurgical-grade silicon. Though the mining of quartz is mentioned, the photovoltaics industry is not expected to have a significant impact on this operation.

It may be debatable whether the starting point for cadmium sulfide cells should be production of cadmium or of cadmium sulfide. Depending on the future market for cadmium sulfide cells, the cadmium requirements for cell production could represent a significant percentage of the total market. Moreover, because the cadmium used in producing cadmium sulfide must be very pure, additional refinement steps and additional workers are needed. For these reasons and because cadmium is a significant toxicological and environmental hazard, cadmium refining is discussed.

Production of both gallium and arsenic is discussed as the starting point for gallium arsenide cells. Manufacture of these cells will significantly affect the production of gallium. Though arsenic production will not be affected to as great an extent, refinement is discussed because of the significance of arsenic as an industrial toxicant.

Except for the final toxicological section each major section of the report is organized into two major parts: a description of the technology, followed by a discussion of the industrial hygiene concerns. The final section reviews the toxicology of materials used for production of the solar cells discussed in Sections 3 through 6.

The appendix consists of reports of the plant surveys conducted by PEDCo and Occusafe.

3. SILICON SOLAR CELLS

Silicon represents by far the major photovoltaic semiconductor material, both in current production and in research and development work (4). Thus it is dealt with most thoroughly in this review. Much of the current production-scale technology for silicon solar cells is carried over from the semiconductor industry. Application of this technology to photovoltaic systems must include a drastic reduction in production costs to make these systems cost-competitive with conventional residential or utility energy systems. A series of studies by the Jet Propulsion Laboratory (JPL) have focused on low-cost silicon solar arrays and, in accord with this objective, on the development of automated arrays assembly (5,6). A number of promising production processes in research and development stages are discussed in this section and evaluated from an industrial hygiene perspective.

Figure 3-1 presents the major sequential steps in production of silicon solar arrays. This sequence is followed by a discussion of the production processes. Many variations on this sequence are possible as indicated in the trip reports for Plants A to I which describe current silicon production technology.

3.1 POLYCRYSTALLINE SILICON PRODUCTION

The two types of silicon generally referred to are semiconductor-grade quality and solar-grade quality. Semiconductor-grade silicon is described as being free of impurities to as low as 1 part per billion (ppb); solar-grade silicon is slightly less pure, and although not suitable for the entire semiconductor industry may possibly be very suitable for manufacturing high-efficiency solar cells (3). Semiconductor and solar-grade silicon represent a very small fraction of the total silicon production; the extreme purity required for these applications has necessitated additional purification steps.

As the first step in production of silicon solar arrays, metallurgical-grade silicon (MG-Si) is produced by reduction of quartzite with coke in an electric arc furnace. The air effluent stream is filtered to remove silicon oxide (SiO) and silicon

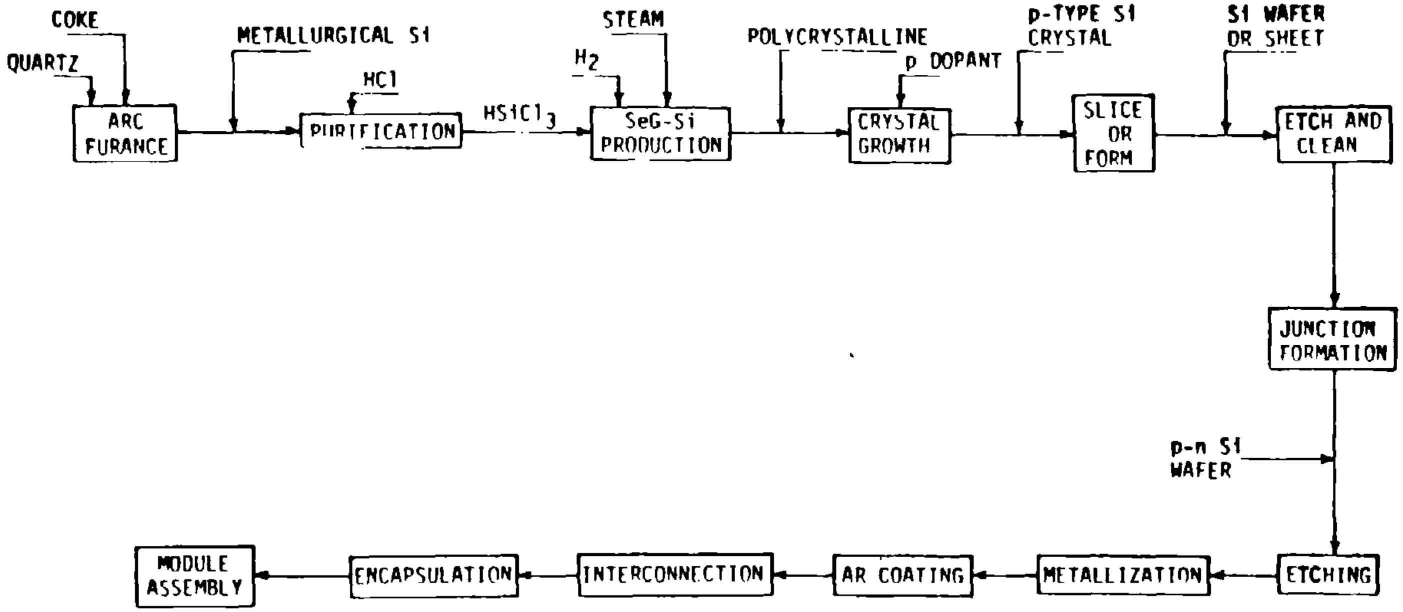


Figure 3-1. Simplified schematic of silicon solar cell module production. (Ref. 1)

fines. The molten MG-Si is drawn from the furnace and blown with oxygen or an oxygen-chloride mixture to reduce the levels of aluminum, calcium, and manganese impurities.

The next step is the production of trichlorosilane. Trichlorosilane ($SiHCl_3$) is produced by fluidizing a bed of fine pulverized MG-Si with hydrogen chloride (HCl) in the presence of a copper-containing catalyst (7). This reaction also produces mono- and dichlorosilane (SiH_3Cl, SiH_2Cl_2), silicon tetrachloride ($SiCl_4$), and hydrogen. The reactor effluent is separated into a silicon dust stream, an exhaust gas stream, and light and heavy silanes fractions. The light silanes stream, mainly SiH_2Cl_2 and SiH_3Cl, is recycled to the reactor. The heavy silanes stream, containing SiH_2Cl_2, $SiHCl_3$, and $SiCl_4$, is fractionated to produce high-purity $SiHCl_3$ for silicon cell production; the SiH_2Cl_2 is recycled to the reactor, and the $SiCl_4$ is sent to storage (8). The $SiHCl_3$ is further treated in the Siemens process, shown in Figure 3-2. A recycled hydrogen stream is saturated with $SiHCl_3$ prior to being fed to silicon rod deposition chambers. Polycrystalline solar-grade silicon (SeG-Si) is produced by chemical vapor deposition onto a single-crystal silicon seed rod under controlled temperature conditions at 1100° to 1160°C (1370°K). The exit gas stream is resaturated with $SiHCl_3$ and recirculated. The deposition rate is very slow (1.44 cm/day), resulting in a 3- to 4-day cycle time for ingot growth. This is a very energy intensive (8,9) step.

A concentrated effort in the LSA project is the development of low-cost alternative processes for SeG-Si production that will reduce the cost from the present $65/kg to $10/kg. By contrast, the cost of MG-Si is about $1/kg. Much of the substantially higher cost of the SeG-Si product is attributable to the $SiHCl_3$ processes (7).

Three major process alternatives for lower-cost production of SeG-Si are being developed. The Union Carbide SeG-Si process begins with the hydrogenation of $SiCl_4$ in a fluid bed reactor to form $SiHCl_3$ at 500°C (932°F) and 3.45×10^3 kPa (500 psig) with a copper catalyst, while consuming MG-Si (9). The reaction is represented as follows:

$$3SiCl_4 + 2H_2 + \text{MG-Si} \overset{Cu}{\rightleftarrows} 4HSiCl_3$$

The $HSiCl_3$ is then redistributed with dichlorosilane (H_2SiCl_2), and $SiCl_4$ in the presence of an ion exchange amine catalyst, as follows:

$$2HSiCl_3 \xrightarrow{\text{catalyst}} H_2SiCl_2 + SiCl_4$$

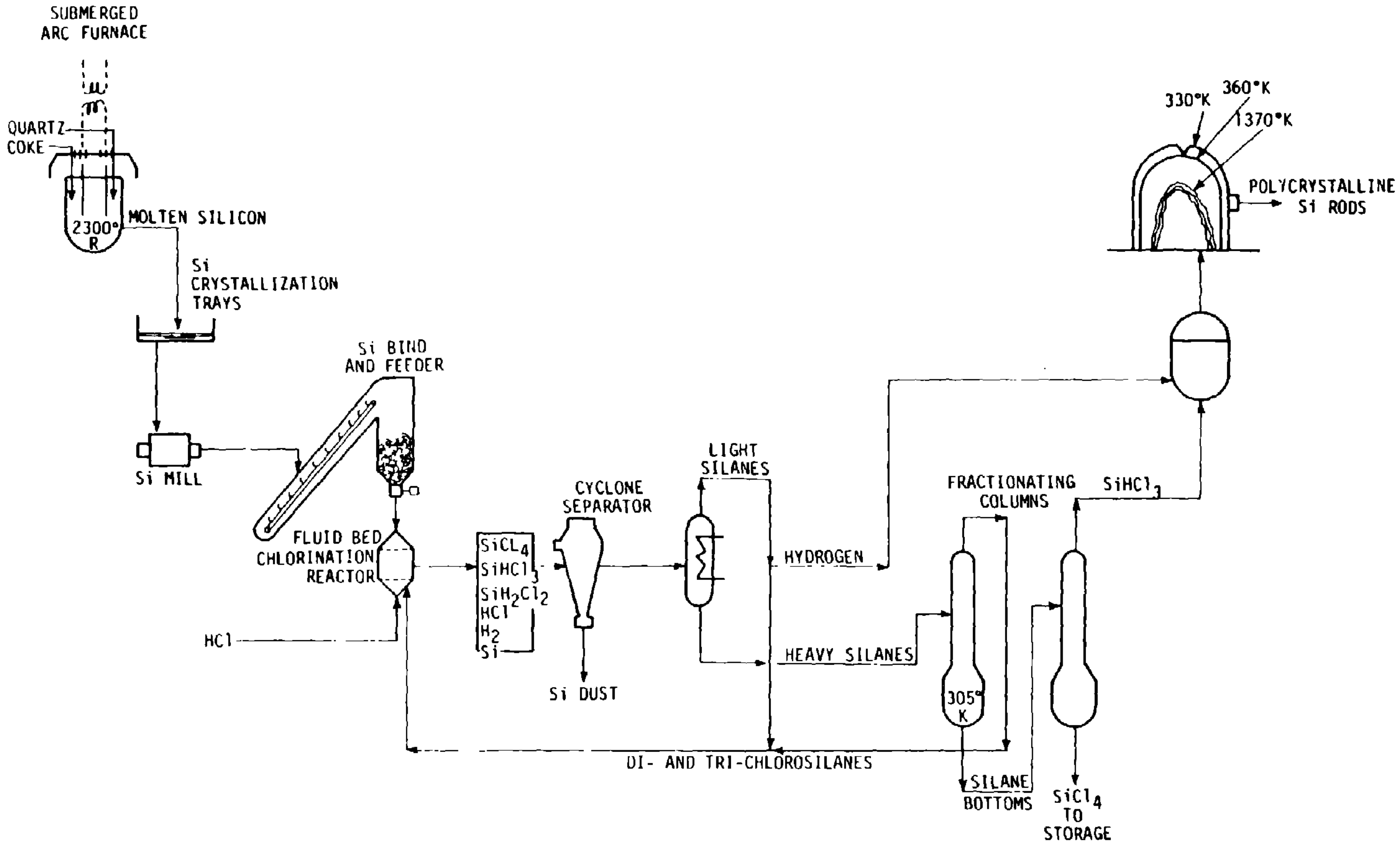


Figure 3-2. Simplified process flow diagram for quartz to polycrystalline silicon production. (Ref. 8)

The H_2SiCl_2 is then redistributed to form silane and trichlorosilane in the presence of the amine catalyst. The net reaction is:

$$3H_2SiCl_2 \xrightarrow{\text{catalyst}} SiH_4 + 2HSiCl_3$$

The trichlorosilane is recycled and the silane is routed to the pyrolysis unit. In the conversion of chlorosilanes to silane, distillation columns are used to ensure the purity of the final silane product.

The pyrolysis unit to be used in the Union Carbide process is a free space reactor into which silane is injected through a port at the top of the apparatus where it is heated to at least 800°C (1472°F). Powdered silicon and hydrogen are formed. The powdered silicon falls to a storage hopper, from which it is transferred into one of two melters, where it is consolidated. A simplified diagram of the equipment is shown in Figure 3-3.

Another process for production of low-cost polycrystalline silica is being developed by SRI International (11). A simplified process flow diagram is shown in Figure 3-4. The process basically involves four steps. In the first step fluosilicic acid (H_2SiF_6) is converted to silicon tetrafluoride (SiF_4). The H_2SiF_6 first enters agitated precipitation vessels with sodium fluoride (NaF) and some NaOH to precipitate silicon sodium fluoride (Na_2SiF_6). This reaction is as follows:

$$H_2SiF_6(ag) + 2NaF(s) \rightarrow Na_2SiF_6(s) + 2HF(ag)$$

The Na_2SiF_6 is separated from the HF on a belt filter and dried.

The second step in this process involves the thermal decomposition of the Na_2SiF_6 in a retort, leading to formation of SiF_4 and NaF. The NaF is recycled and used in the first step discussed above. The chemical reaction in this step is as follows:

$$Na_2SiF_6(s) \xrightarrow[650°C]{\text{Heat}} SiF_4(g) + 2NaF \text{ (Recycle)}$$

The next process step involves the reduction of SiF_4 with sodium, as follows:

$$SiF_4(g) + 4Na \rightarrow Si(s) + 4NaF(s).$$

The reduction of SiF_4 with sodium is a highly exothermic reaction and is the critical step in the process. The reaction occurs in reduction pots, which are air-cooled after the reaction is complete The resultant Si/NaF sponge is removed from the pots and transferred to a ball mill, where it is crushed into a powder.

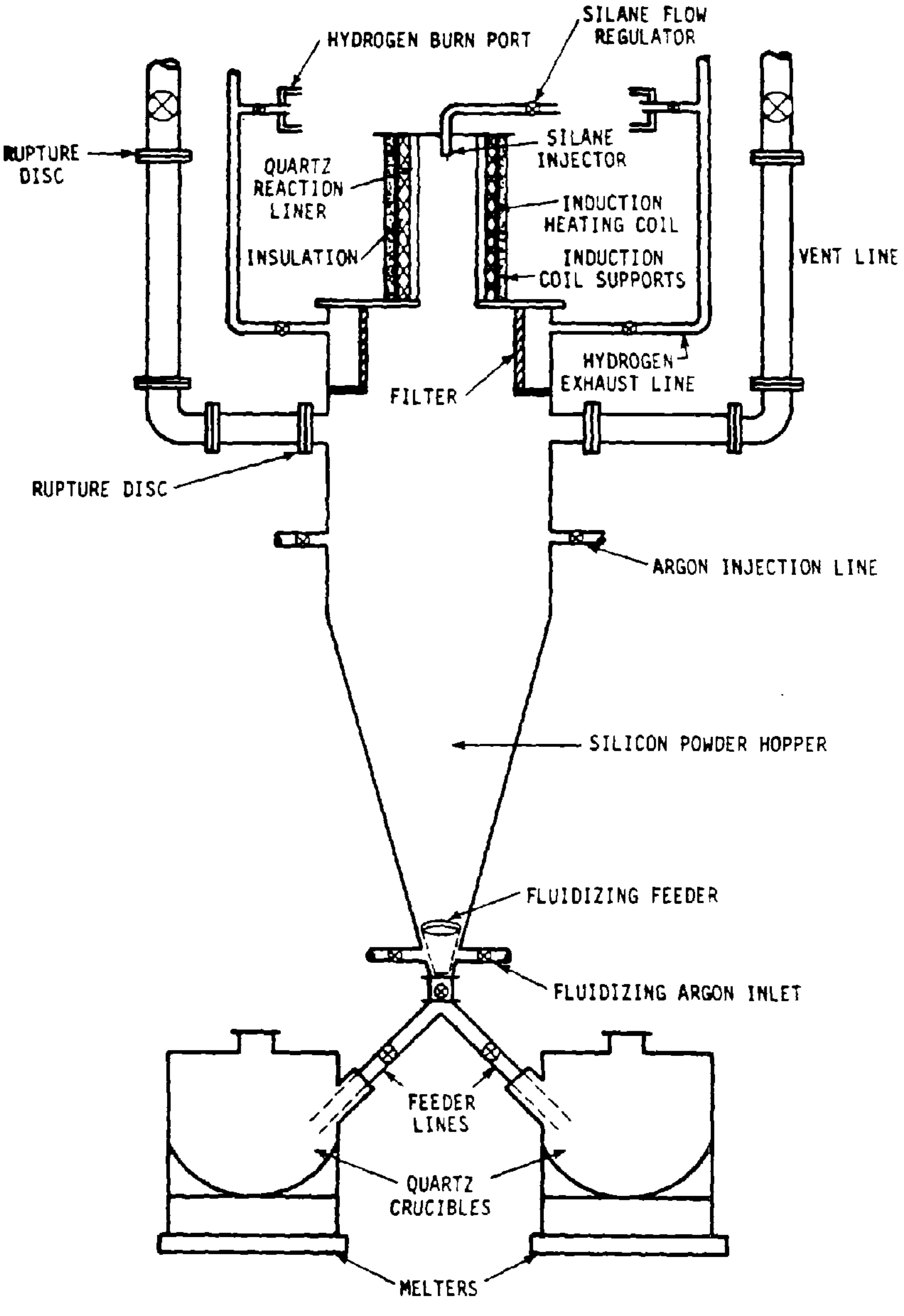


Figure 3-3. Free-space reactor, hopper, and melters for polysilicon production (Ref. 10)

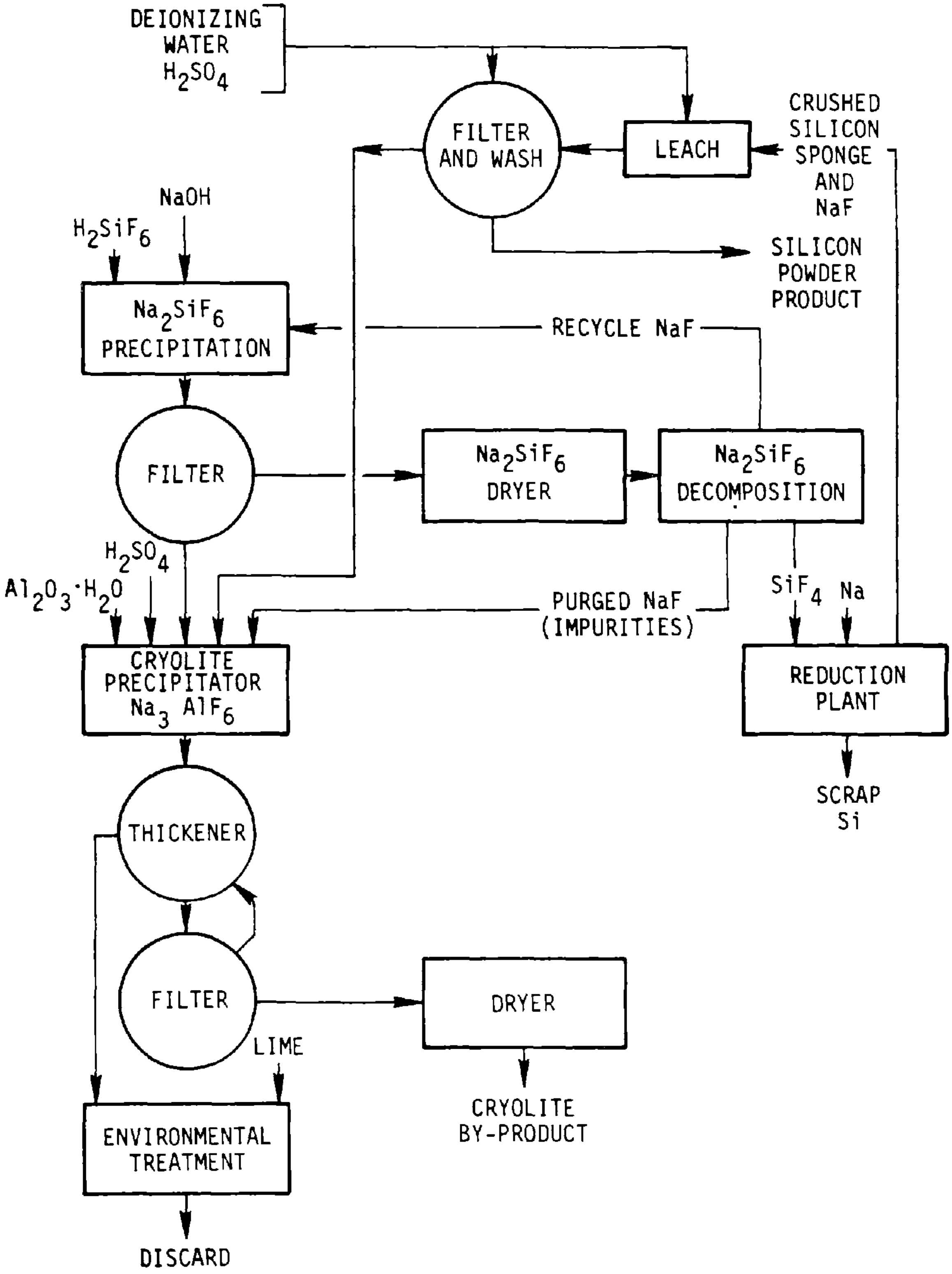


Figure 3-4. SRI silicon process - block flow sheet (Ref. 11)

The next process step involves leaching the Si/NaF powder with a sulfuric acid solution to remove the NaF, in the following chemical reaction:

$$\mathrm{Si} + 4\mathrm{NaF} \xrightarrow[\text{leach}]{H_2SO_4} \mathrm{Si(s)} + 4\mathrm{NaF(aq)}$$

The powder is first agitation-leached briefly and then pumped to filter presses, where it is thoroughly leached and washed prior to discard of the silicon cake. The clean silicon powder is then discharged to a vacuum dryer.

Because the markets for NaF and HF are relatively small, and the disposal of these as wastes could cause potential environmental problems, it was decided that these byproducts of the process could be used to manufacture synthetic cryolite (Na_3AlF_6), which is used extensively for electroreduction of aluminum from alumina. Thus the next process step is the precipitation of cryolite, as follows:

$$4\mathrm{NaF} + 2\mathrm{HF} + \mathrm{Al(OH)_3} + 1/2\ H_2SO_4 \rightarrow Na_3AlF_6 \downarrow + 1/2\ Na_2SO_4 + 3H_2O$$

Since the excess HF formed in the first process step is insufficient for precipitation of cryolite, sulfuric acid is used to make up the additional acid.

Westinghouse has developed another promising process whereby molten silicon of SeG-Si purity is produced in an arc-heated hydrogen-argon environment by the sodium reduction of $SiCl_4$. The $SiCl_4$ is formed by reaction of silicon carbide (SiC) with chlorine gas and is purified by distillation. Both sodium and chlorine are produced by electrolysis of coproduct NaCl in gaseous form (12).

A diagram of the reactor is shown in Figure 3-5. Liquid sodium is first sprayed through a nozzle, which breaks the stream into small droplets. The droplets of sodium are entrained within an arc-furnace-heated stream of hydrogen-argon gas at a ratio of 4:1. This results in vaporization of the droplets. Just downstream of the arc heater, $SiCl_4$ is injected. The reaction occurs rapidly, and the silicon product is separated in the form of silicon condensate collecting on the surfaces of the reactor walls (12). The thin film of molten silicon collected on the walls then runs down by gravity to a quartz-lined collecting crucible.

Other processes for production of SeG-Si are being developed by Motorola, Battelle, and Dow Corning. The technological potential for large-scale silicon production by these processes is reportedly not as advanced as in the three processes discussed above.

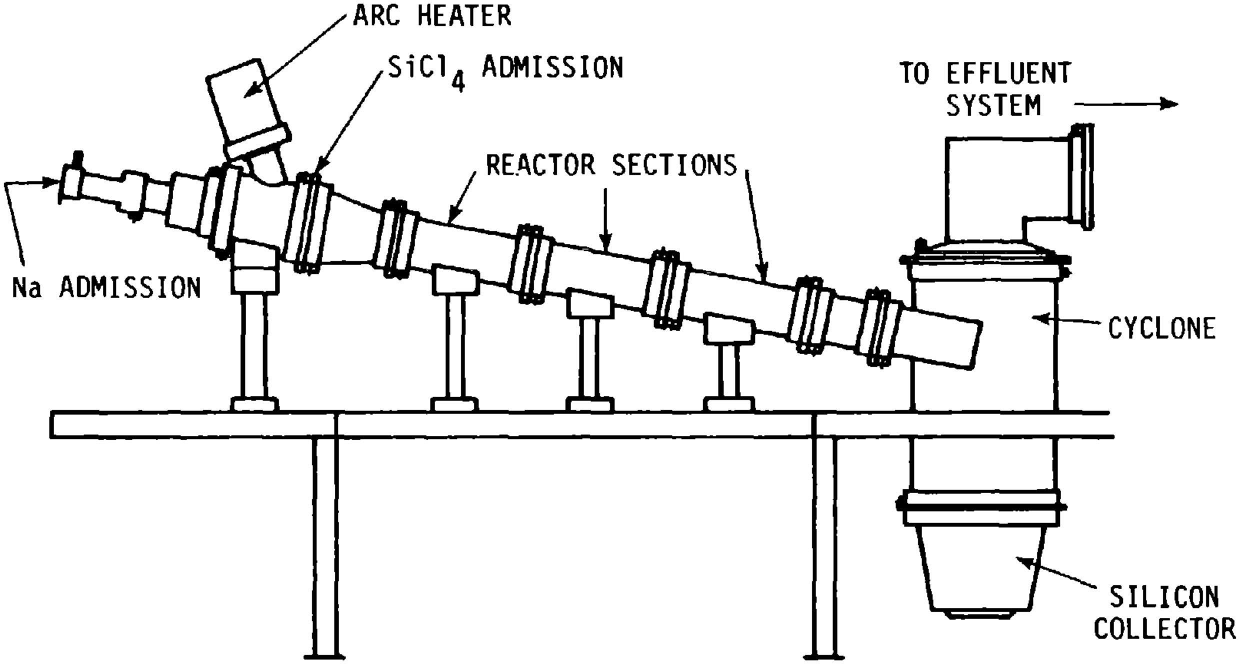


Figure 3-5. Side view of silicon reactor assembly.(Ref. 12)

The Motorola process involves conversion of MG-Si in a three-step silicon difluoride (SiF_2) polymer transport purification process. Reaction of MG-Si with SiF_4 forms gaseous SiF_2 at 1350°C (2462°F). This is converted to a polymeric form under cryogenic conditions -45° to -100°C (-50° to -150°F) and finally converted to SeG-Si at 360° to 805°C (680° to 1481°F). The last process step also forms SiF_4 and higher homologues (13).

The Battelle process involves the addition of zinc to $SiCl_4$ in a fluidized bed reactor. This results in the formation of Si and zinc chloride ($ZnCl_2$). The $ZnCl_2$ is recycled back to zinc by passing it successively through a condenser, an electrolysis cell, and a vaporizer. The zinc is used again in the reaction with $SiCl_4$ (14).

The Dow Corning process involves producing liquid silicon by feeding high-purity quartz and carbon into a direct-arc furnace, followed by purification to SeG-Si by Czochralski crystal-growing technology. The purification involves undirectional solidification of silicon to reduce impurity levels in the resulting polycrystalline silicon (SeG-Si) (15). A major drawback of this process is the difficulty of procuring a high-purity carbon source compatible with the process.

3.2 PREPARATION OF SINGLE-CRYSTAL SILICON WAFERS

The SeG-Si is normally converted to single-crystal form to improve the efficiency of the conversion of sunlight to electrical energy. Single-crystal silicon cells reportedly operate commercially at 10 to 13 percent efficiency, with a probable maximum achievable efficiency of 20 to 22 percent (4). The major commercial crystal-growing technique is the Czochralski (Cz) process, which produces cylindrical ingots ranging from 5 to 15 cm (2 to 6 in) in diameter and weighing from 9 to 36 kg (20 to 79 lb) each (8). In this process polycrystalline SeG-Si broken into small chunks and a dopant, commonly boron, are melted in a quartz crucible and a seed silicon crystal is introduced. Given an argon or helium atmosphere with controlled temperature and controlled rotation of the crucible, the crystal is slowly withdrawn at a controlled rate to pull the cylindrical single-cell silicon into the crucible. Figure 3-6 presents a schematic of a Cz crystal puller.

A major inherent limitation of the Cz process is that the ingot must be sliced into circular wafers, and because of sawing losses and imperfections only about 20 percent of the ingot is suitable for wafers (7). An attendant problem is that production-scale operation is on a batch basis, which necessitates replacing

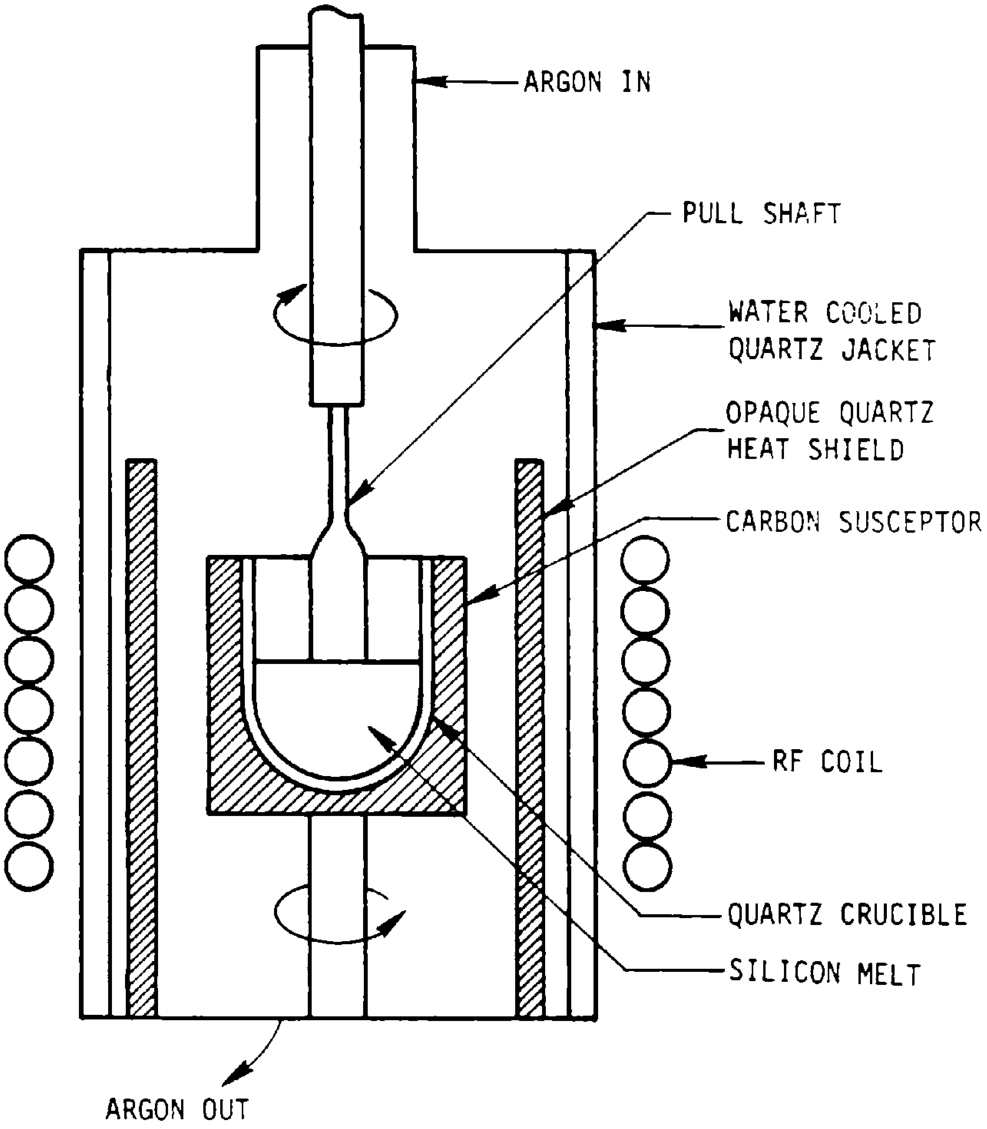


Figure 3-6. Schematic of Czochralski crystal puller (Ref. 19)

the quartz crucible and cleaning all exposed surfaces between runs. A continuous crystal-growing process is being developed that should reduce losses and possibly reduce dust generation by reducing the frequency of replacing the quartz crucible. Production of single ingots of up to 100 kg (220 lb) from the same crucible has been reported (16).

Extensive research and development is being aimed at alternative single-crystal SeG-Si technologies, mainly through ribbon and sheet growth processes. The major processes are listed in Table 3-1. An inherent advantage of these processes is that the thickness of the silicon ribbon or sheet can be controlled. No sawing is needed, and as a result the silicon usage is potentially far lower. These technologies are briefly described below:

1. Ribbon growth is done with shaping dies that are either wetted (edge-defined film-fed growth, EFG; and capillary action shaping techniques, CAST) or nonwetted (Stepanov technique) (17). In these processes, the die defines the ribbon shape.

2. Self-shaping web-dendrite growth processes control the ribbon dimensions not with a die but by the seed crystal characteristics and silicon melt temperature (17).

3. Laser zone crystallization growth uses a laser heat source, which zone-melts in the region where the laser beam is focused, producing continuous crystal structure (17). Preformed polycrystalline silicon ribbon is required, and auxiliary heating is used in the pre- and post-melt ribbon areas. The use of high-power CO_2 lasers is reported (18).

4. Dip-coating involves forming a crystalline silicon coat on the surface of a ceramic sheet substrate being pulled from a silicon melt (17).

5. Chemical vapor deposition (CVD) growth of silicon is the thermal decomposition of silane (SiH_4) or a chlorosilane compound in a hydrogen atmosphere on a substrate. Single polycrystalline materials have been used as substrates, and a floating substrate technique uses molten tin (17).

Although ribbon and sheet growth techniques can produce silicon directly in the thickness needed for array processing, the silicon ingot from the Cz process may be cut into wafers in the following process steps:

TABLE 3-1. CRYSTAL GROWTH TECHNOLOGIES

Laboratory	Research and Development Area
Ribbon Growth Processes	
Mobile-Tyco Waltham, Massachusetts	Edge-defined film-fed growth (EFG)
IBM Hopewell Junction, New York	Capillary action shaping technique (CAST)
Univ. of So. Carolina Columbia, S. Carolina	Web-dendritic growth
Westinghouse Pittsburgh, Pennsylvania	Web-dendritic growth
RCA Princeton, New Jersey	Inverted Stepanov growth
Motorola Phoenix, Arizona	Laser zone crystallization
Sheet Growth Processes	
Honeywell Bloomington, Minnesota	Dip-coating (on low-cost substrates)
Rockwell Anaheim, California	Chemical vapor deposition (on low-cost substrates)
General Electric Schenectady, New York	Floating substrate growth (chemical vapor deposition on liquid tin)
Univ. of Pennsylvania Philadelphia, Pennsylvania	Hot-forming of silicon
Ingot Growth and Cutting	
Crystal Systems Salem, Massachusetts	Heat-exchanger ingot casting (HEM) and multiple-wire sawing
Texas Instruments Dallas, Texas	Czochralski ingot growth and multiple-blade sawing
Ingot cutting	
Varian Lexington, Massachusetts	Multiple-blade sawing

(Reference 16)

1. The seed end of the ingot is chopped with a single-blade diamond saw and etched in concentrated HNO_3-HF-acetic acid, followed by rinses and a milder etch to both ends (19).
2. The ingot ends are inspected for crystal imperfections and orientation.
3. The opposite end of the ingot is ground.
4. The ingot diameter is ground round.
5. A lap is ground longitudinally and the ingot is bonded to a ceramic submount with hot melt adhesive or wax (8).
6. The ingot is cut into wafers. Currently single slices are cut with an internal diameter diamond blade using a water coolant (17,20).

This process is slow and results in high silicon losses (kerf loss) (17); these disadvantages have spurred developmental work on multiple-blade or wire ingot cutting saws, which are used with an abrasive slurry consisting of silicon carbide grit in a mineral oil base suspension containing fine clay (8,21, and personal communication with Dr. James Lui, JPL, Feb. 5, 1979).

Another method of shaping being investigated is laser scribing. Little information is available on this process.

3.3 SILICON ARRAY ASSEMBLY

The silicon array production phase includes the processing steps involved in production of finished modules starting with the silicon wafer or sheet material. A number of alternative techniques are being developed for each processing step. The processes that appear to have commercial potential in the 1980's are discussed in this section. Figure 3-7 shows a generalized process sequence and the process alternatives to be discussed here. The following process descriptions are presented in the sequence shown in the figure, although many alternative sequences are possible.

3.3.1 Surface Cleaning or Etching

Most cell manufacturing processes must include cleaning and etching steps. Wafers from Cz-grown ingots initially must be etched and cleaned to remove saw damage. These steps are also needed in production by other processing sequences. Surface cleaning and etching techniques can be classified as chemical and mechanical.

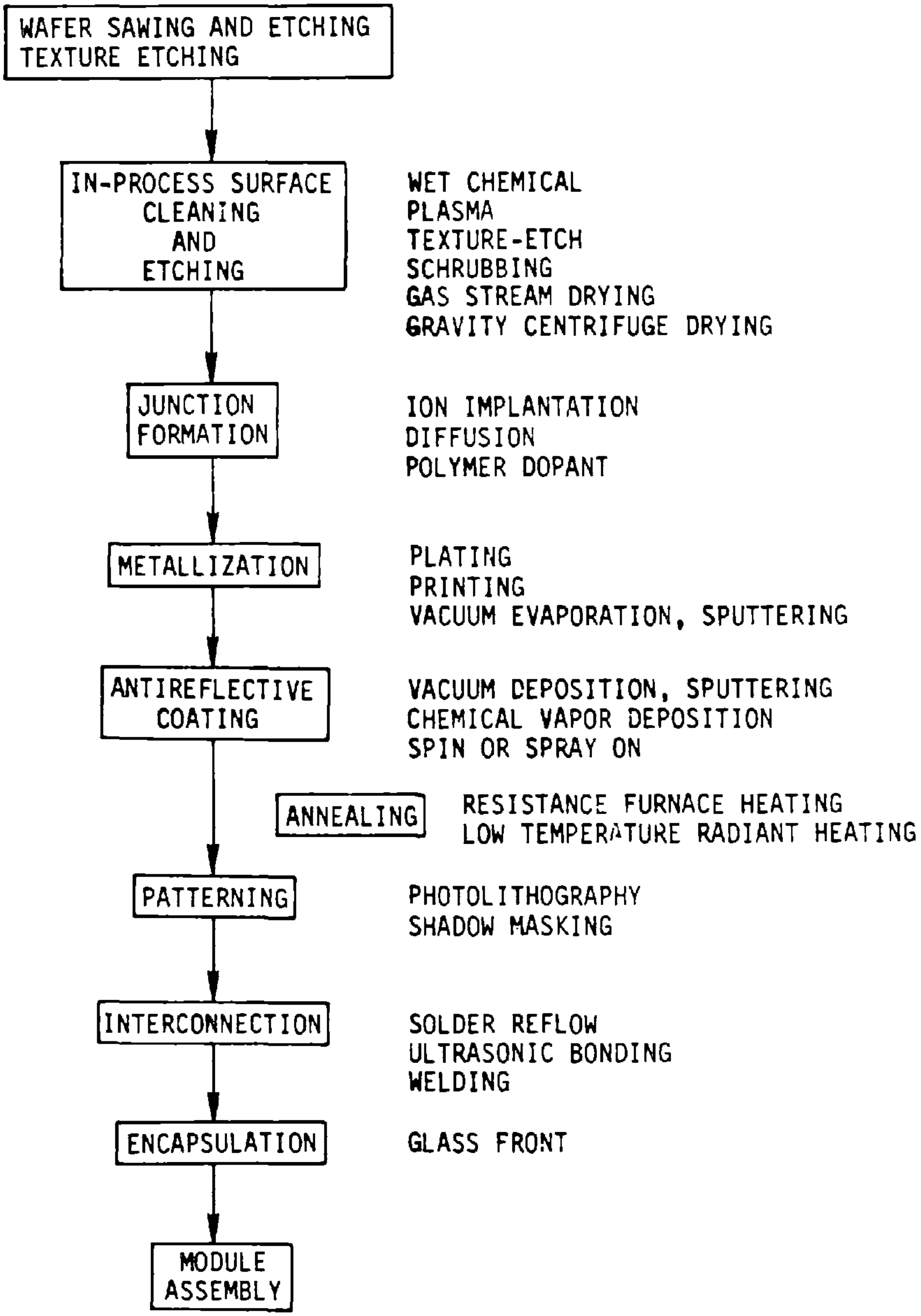


Figure 3-7. Major processing steps in silicon array assembly.

Wet Chemical Cleaning and Etching--

The wet chemical processes usually make use of water-based acids and bases and organic solvents. Sawed Cz wafers may initially be etched in 30 percent NaOH, then given a water rinse, a 1 percent NaOH etch, and a second water rinse. Also, a concentrated HF-acetic-nitric acid solution (20) or sequential nitric acid and sulfuric acid baths (22) may be used, followed by a water rinse. In one operation wafers are cleaned in a mild soap solution, dilute KOH, methanol, and a Freon degreaser prior to etching (23). Normally, wafers are cleaned after the initial etch. One plant reported using a mixture of H_2O_2-H_2SO_4 for cleaning (24). Organic solvent cleaning techniques are best suited for removal of organic residues (25). Among organic solvents reportedly in use are methanol; 1,1,1-trichloroethane; acetone; isopropyl alcohol (26); and trichloroethylene (27). After junction formation by diffusion, an outer SiO_2 layer is removed by a hydrofluoric-nitric (HF-HNO_3) acid etch to expose the p-layer (8). In addition to HF and HNO_3 fumes, this etch causes formation of an SiF_4 contaminant (8).

Following is a typical sequence of operations involved in an etching operation:

Receive cassettes from receiving inspection.

Load and immerse the cassettes in the etching solution for the designated time.

Move the cassettes for rinsing and cleaning.

Dry the wafers.

Transport the cassettes from drying (28).

In some cases, wafer damage may be removed by polishing and followed by a final cleaning (20). In one plant, a dip sequence of triton-X, ammonium hydroxide, and water is used (20). In another plant, the polished slices are cleaned in hot dilute nitric and sulfuric acids, a series of cascades of hydrofluoric acid and ammonium hydroxide, and a final Freon wash (29). Liquid wastes containing acids and bases must be neutralized; other liquid wastes must be degraded before disposal or must be recovered, purified, and recycled to the process.

Plasma Cleaning and Etching--

The use of plasma for etching metals, semiconductor materials, and dielectrics in the manufacture of microelectronic products is an established technology (30). Plasma processing has several advantages over wet-processing procedures. First, it is a dry process and uses less expensive chemicals. The necessity for consumption of deionized wate in wet processes has made plasma processing particularly attractive. Plasma etching also provides finer resolution, sharper etching, and less undercutting than can be obtained with chemical etchants (30), and makes possible sequential etching and stripping operations in the same machine; therefore it is more readily applicable to automation than wet processes (30). Also, photoresists, coatings, and masks used in wet chemical processes can be used in plasma processing.

A plasma is similar to a gas except that some of the atoms or molecules of a plasma are ionized and may contain a substantial number of free radicals. Figure 3-8 shows a plasma-system reactor during an etching process using Freon 14 (carbon tetrafluoride or tetrafluoromethane). The typical reactor consists of a cylindrical vessel of aluminum, quartz, or glass; a radio frequency (RF) source; and a control module to control processing time, composition of reagent gas, flow rate of gas, and RF power level (30). In a plasma processing system it is desirable to generate a plasma rich in free radicals, since these radicals move out of the region where the plasma is generated (30). If this can be done, the component being etched can be treated outside the plasma-generating region, allowing a greater degree of control and a more precise etch (30).

Anisotropic plasma etching with silicon has been reported (26). Also the use of CF_4 and HF has been reported (28). As shown in Figure 3-8, use of CF_4 will result in the formation and possibly the low-level emission of SiF_4 (30).

Texture Etching--

Surface texturing improves the performance of solar cells by reducing incident light reflection and improving metal adhesion. The use of sodium hydroxide has been reported in a sequence that included a "flash" etch, rinse, and sequential 5-minute cleanings in hot trichloroethane and methanol, respectively (26). A heated KOH-based solution may also be used for texture etching (24), as can plasma etching (26). A hot NaOH etchant is an alternative to the more conventional HF-HNO_3-acetic acid etchant (6).

Wafer Scrubbing--

Wafers can be cleaned by mechanically scrubbing the surface. This procedure is particularly suited to removal of particulate matter and is easily automated. Ultrasonic cleaning can be used to augment any chemical cleaning techniques (25).

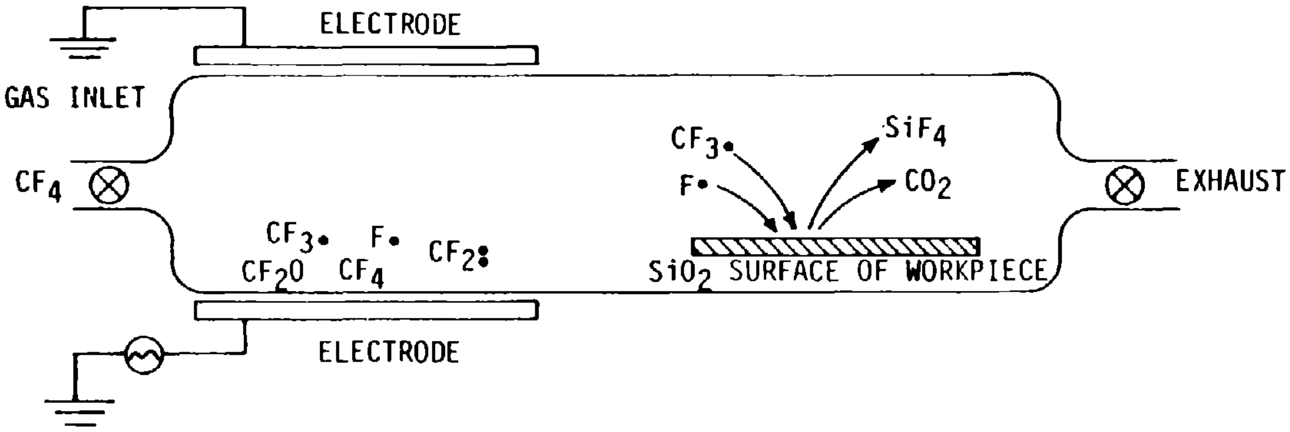


Figure 3-8. A plasma-system reactor during an etching process.

The plasma is generated in the space between the two electrodes. The workpiece (a wafer bearing a surface layer of SiO_2) lies outside of the plasma region. Free radicals ($CF_3\cdot$ and $F\cdot$) survive to reach the wafer and react with the SiO_2 to produce SiF_4 and oxygen. Other reactive particles perish before they can reach the workplace. (Ref. 30)

Drying Operations--

Gas stream drying and gravity centrifuge drying are the two drying methods that appear feasible. Gas stream drying is the more likely alternative for processing of sheet silicon (31) and could be automated on a conveyor (28).

3.3.2 Junction Formation

Junction formation involves the most complex and critical steps in solar cell processing and necessitates stringent control of the formation techniques (31). Diffusion processes are the most fully developed; ion implantation and polymer dopant applications are promising alternatives. Different process steps and sequences are possible in each of these processes. For example, in diffusion processes a mask can be applied to the wafer back surface and subsequently etched off after diffusion, or the wafer can just be etched on the back surface after diffusion (28).

Diffusion-CVD--

Diffusion refers to chemical vapor diffusion (CVD) or open-tube diffusion, although the polymer dopant process also involves wafer diffusion for junction formation. An n-doped layer of material is formed on the wafer by diffusing phosphorous into the crystal structure in a tube furnace under controlled temperature and time conditions. The operating cycle consists of pulling the wafers in quartz boats into the furnace, maintained in an argon or nitrogen atmosphere. After the furnace reaches temperature equilibrium, a controlled flow of a phosphorous gas, usually phosphine (PH_3) or phosphorus oxychloride ($POCI_3$) and oxygen, is introduced. The phosphorus reacts with oxygen to form phosphorus pentoxide (P_2O_5), which then reacts with the wafer surface to form a glassy SiO_2 layer while part of the phosphorus diffuses into the silicon (8,31). The exit gas from a process using PH_3 dopants includes phosphorous pentoxide, and phosphoric acid (H_3PO_4) (8). The chloride species in the exit gas from use of $POCl_3$ dopant are not reported. If a p-doped layer is to be formed, boron trichloride (BCl_3) is used as a boron dopant source (17,18, 20,21,25,28,31,32). After dopant addition, a temperature cycle is completed at 800° to 1000°C (1472° to 1832°F) (32). A negative pressure gradient is maintained between the inlet where wafers are loaded and the exhaust from the tube furnace (8). A ventilation takeoff is located by the tube inlet (22). One reported cycle includes 10 minutes preheat in N_2, 45 minutes with $POCl_3$ flowing by a programmed puller (32), and 10 minutes in N_2-10 percent O_2 while the wafers are slowly withdrawn.

In an alternative diffusion technique, wafers are placed back-to-back in quartz cassettes for diffusion; after diffusion and cooling, their positions are reversed so that the diffused surfaces are facing each other. This is done to prepare the cassettes for back etching of the wafers without removing the junction in the front. A plasma etch with anhydrous HF and CF_4 was reported (28). An alternative cell back preparation technique for low-cost production involves application of an aluminum powder, mixed with a binder and a solvent before diffusion. The surface is textured, and then during diffusion the aluminum forms an alloy with the back material and creates a p^+ surface (3). Normally the unwanted junction on the back surface is etched away in an expensive sequence of masking, etching, rinsing, mask removal, and drying (6).

Systems are available that provide automated control of the diffusion atmosphere as well as automated pulling of the quartz boat into and out of the furnace tubes.

Ion Implantation--

In ion implantation ion beams are used to implant the high-purity dopant, the depth depending upon implantation energy (31). With the use of high-current ion implants (100 mA), the implant time per wafer can be reduced to seconds (26); the largest machines, however, are on the order of 3 to 4 mA (3). The automation potential for high-rate production with this process is reportedly very high. Designs have been produced of a 100-mA machine configuration that is compatible with the LSA program objectives (3).

The standard approach for implantation of wafers involves manually loading a carrousel of wafers or cells on individual stations. The carrousel is drawn into the vacuum chamber, which must then be pumped down before the wafers are implanted sequentially as they are rotated. The implanting causes an amorphous surface layer to form on the cell, which is removed by high-temperature annealing for 15 to 45 minutes at 900° to 1000°C (1052° to 1832°F). Laser annealing may prove to be a more attractive technique (26). Dopants reported are phosphorus, arsenic, and boron (22), usually by use of phosphine (PH_3), arsine (AsH_3), and boron trifluoride (BF_3) respectively (29). It is reported that phosphorous hexafluoride (PF_6), and arsenic hexafluoride (AsF_6) are used as sources for phosphorous and arsenic (33). Both n-type and p-type dopants can be implanted simultaneously, with the n-type and p-type and the p-type on the back; and the p-dopant can be driven in during annealing (22). Pulsed annealing by an electron beam also appears to be a promising candidate process for low-cost cell production (3).

Polymer Dopants--

Application of dopants in liquid or paste form is an alternative to vapor-phase diffusion. The application can involve spin-on, roll-on, or screening techniques (34). The use of spin-on sources may be restricted to wafer diffusion (31). Typical spin-on sources consist of a solution of an organic silicate, an alcohol, and a small proportion of an organic compound of the desired dopant element. The solution is sprayed from an orifice onto the wafer rotating on a palette, to produce a uniform liquid film. Because excess liquid is spun off, this procedure results in relatively high usage of chemicals. Subsequent heat treatment forms a doped SiO layer on the surface of the wafers while the organic components are driven off (31). Phosphorus, arsenic, and boron dopant sources have been used (34). For this aqueous dopant sources that would reduce emissions have been developed. Polymer dopants containing P_2O_5 and P_2O_3 are reported (personal discussion with Don Bickler, Brian Gallagher, et al., JPL, Feb. 5, 1979). Other spin-on dopants reportedly used are tetraethyl orthosilicate, triethyl borate, and pentaethyl phosphate (133). Roll-on screening techniques are described under metallization. They offer an advantage over spin-on techniques in that chemical usage should be reduced. Exact chemical formulations are not known.

3.3.3 Metallization

The metallization grid is used for current collection. The metallized portion should cover a minimum area on the front surface to achieve a minimum resistance (31). Processes can be categorized as vacuum and nonvacuum; the latter includes plating and printing which are generally two separate operations for front and back metallization or contact application.

Vacuum Metallization--

Vacuum processes include evaporation and sputtering technologies. They are not preferred for low-cost processing because not all of the metal can be directed onto the substrate. Less than 5 percent of the metal that condenses on the front side is used in the metallization pattern, and throughput is low (25,31). The metal may be vaporized by thermal heating, by an electron beam, or by RF discharge. The front pattern is defined by evaporation through a metal mask or photolithographically. Metals that have been used include silver (27,35) and sequential layers of titanium-palladium-silver (36). The layers are then sintered. The titanium-palladium-silver metal evaporation process is currently the most reliable and also the most expensive (6).

Plating Metallization--

Electroless plating, primarily with nickel, is a well developed technology amenable to automation. A gold layer may be added to increase contact reliability (6). A proposed process sequence for low-cost production starts with screen printing and drying of a wax on each side to form the pattern-defining mask. Cells are then placed into a sequential tank dipping machine. First HF is used to etch away the glossy layer from diffusion, on both sides, through the mask openings. The cells are then rinsed, immersed in a sensitizing solution, rinsed, immersed into the electroless gold, rinsed, immersed into the electroless nickel, and rinsed. The cell is then placed in a vapor degreaser to remove the wax mask (6).

Printing Metallization--

Printed contacts using screen printing are painted directly onto the silicon solar cell surface and then fired at high temperatures, above 800°C (1472°F) (25). This process is amenable to automation. Typically, the present metal systems are either copper- or silver-based, with 5 to 15 percent of glassfrite and a carrier or binder (composition unknown)(31). Following is a proposed sequence of thick filmprinting for low-cost metallization:

> "This process step receives wafers in a continuous mode on a conveyor and successively prints and dries a back contact. The wafers are then turned front to back with relatively simple handling equipment, and a front contact is screen printed to each wafer successively. The two contacts are then fired simultaneously if they are both of the same material (silver) or they may require separate firing stages if the back contact is not the same material."(28)

In another process a commercial aluminum ink is used to metallize the backside, followed by a second printing with silver ink coating (34). When a thin metallization layer is applied, a solder is added thick enough to act as the primary current-carrying metal. The use of silver-tin-lead solder baths is reported (22). Soldering should lend itself to automation.

When a back p^+ surface is formed, the edge on the junction is short-circuited front to back and cells must be edge-trimmed. Laser cutting with cassette-to-cassette automatic machines is a suggested low-cost technique (6).

3.3.4 Antireflective Coating

Antireflective (AR) coating systems are used to maximize solar cell efficiency and in some cases also for p-n junction passivation. The coating processes of interest for low-cost production are vacuum deposition, chemical vapor deposition, and spin-on, spray-on, or paint-on techniques.

Vacuum Deposition--

Vacuum deposition is similar to vacuum metallization except that patterning is seldom required. Several materials have been used, including evaporated SiO, Ta_2O_5, and SiO-Ta_2O_5 mixtures (25).

Chemical Vapor Deposition (CVD)--

Silicon nitride (Si_3N_4) is used as an AR coating because it has a good refractive index and is the best-known p-n junction passivant (31). The Si_3N_4 is deposited from the reaction of SiH_4 and NH_3 in a nitrogen carrier gas at 600°C (1117°F) in a hot well, quartz-lined furnace (31). A reported process sequence includes depositing Si_3N_4 by low-temperature CVD in a "soft" state and transforming the Si_3N_4 into a high-density state by a modest thermal cycle (31). Throughput is currently limited (31).

Spin-On, Spray-On, or Paint-On--

These techniques are similar to those of polymer dopant processes and printing metallization. Coatings with SiO-TiO_2 (8) and Ti $(OC_3H_7)_4$ (33) are reported, as well as a coating of Ta_2O_5 (31). These techniques are normally followed by patterning and thermal densification. If the coating is applied after metallization, annealing must be done at a lower temperature [250°C (482°F)] instead of 925°C (1697°F) (31). Spin-on techniques do not appear suited for use with rectangular or other sheet silicon materials (31).

3.3.5 Annealing

Annealing is discussed separately because all solar cell manufacture requires some high-temperature annealing.

Resistance Furnace Heating--

Heating with a resistance furnace is proven technology in wide current use. Automated processing should reduce energy consumption (31).

Laser and Electron-Beam Heating--

Processes using lasers and electron beams are developing technologies. Laser heating can be used in any atmosphere, whereas use of electron-beam heating is restricted to a vacuum (31).

3.3.6 Module Assembly

When production of the individual cells is completed, they are assembled into an array or module. Although much of this assembly is now done manually, several studies indicate that much of the procedure could be automated with substantial reductions in cost.

Two basic approaches to module assembly are practiced (26). One involves the direct assembly of individual cells in a module fixture; the other incorporates an intermediate subassembly step, in which individual cells are series-connected into strings and the strings are then arranged in the module. The latter is presently the preferred assembly method (26). Table 3-2 lists advantages and disadvantages of both methods. A simplified flow diagram of a sequence for the subassembly method is shown in Figure 3-9. An exploded view of one proposed module is shown in Figure 3-10. Figure 3-11 shows three-dimensional and cross-section views of another proposed module design.

Present estimates indicate that module assembly will account for approximately $0.285 of the total cost of $1.945/watt, or 14.65 percent (6).

Two major processes are involved in module assembly: interconnection and encapsulation. These processes are discussed below.

Interconnection--

Interconnections are extremely important because poor interconnections can lead to substantial series resistance and subsequently to reduced performance of the module. Experience in the semiconductor industry has shown that metal connections are the most likely failure mechanisms.

Although soldering and welding may be done manually, this is not feasible if the long-term objective of $0.50/Wp for a solar module is to be realized. Several automated methods of interconnecting have been proposed. At present the most promising is solder reflow, a technology already proven in the semiconductor industry (26,28,31). With solder reflow it is possible that all interconnects in one module could be made simultaneously (28,31). Lockheed (26) evaluated three process alternatives for solder reflow: conventional oven heating, induction heating, and vapor-phase heating. Although not yet tested for solar array assembly, vapor-phase heating appears promising because solder flux would not be required. Lockheed has reported successful reflow soldering of circuit boards using solder preforms without flux (31). Texas Instruments has also proposed using a vapor-phase solder reflow unit (condensation soldering) for interconnection (25).

TABLE 3-2. COMPARISON OF MODULE ASSEMBLY METHODS

Assembly method	Advantages	Disadvantages
Direct assembly of cells at module level	Interconnect pattern cut from one piece	High waste of interconnect material
	Mass soldering technique possible	Probable high energy consumption for mass soldering
	Fewer operations	Mostly sequential (lower production rate)
		Quantity of complex fixtures in circulation through most of assembly operations
Subassembly of cells into strings; assembly of strings into module	Many simultaneous operations (higher production rate)	Greater number of operations, therefore more process parameters to be controlled
	Individual spot application of heat to make solder joints (lower energy consumption)	Probable higher equipment investment
	Greater modularity of assembly equipment; downtime reduced by quick replacement of modular units; lower investment in standby equipment	
	Simple modification to accommodate process and/or design changes	

Ref. 26

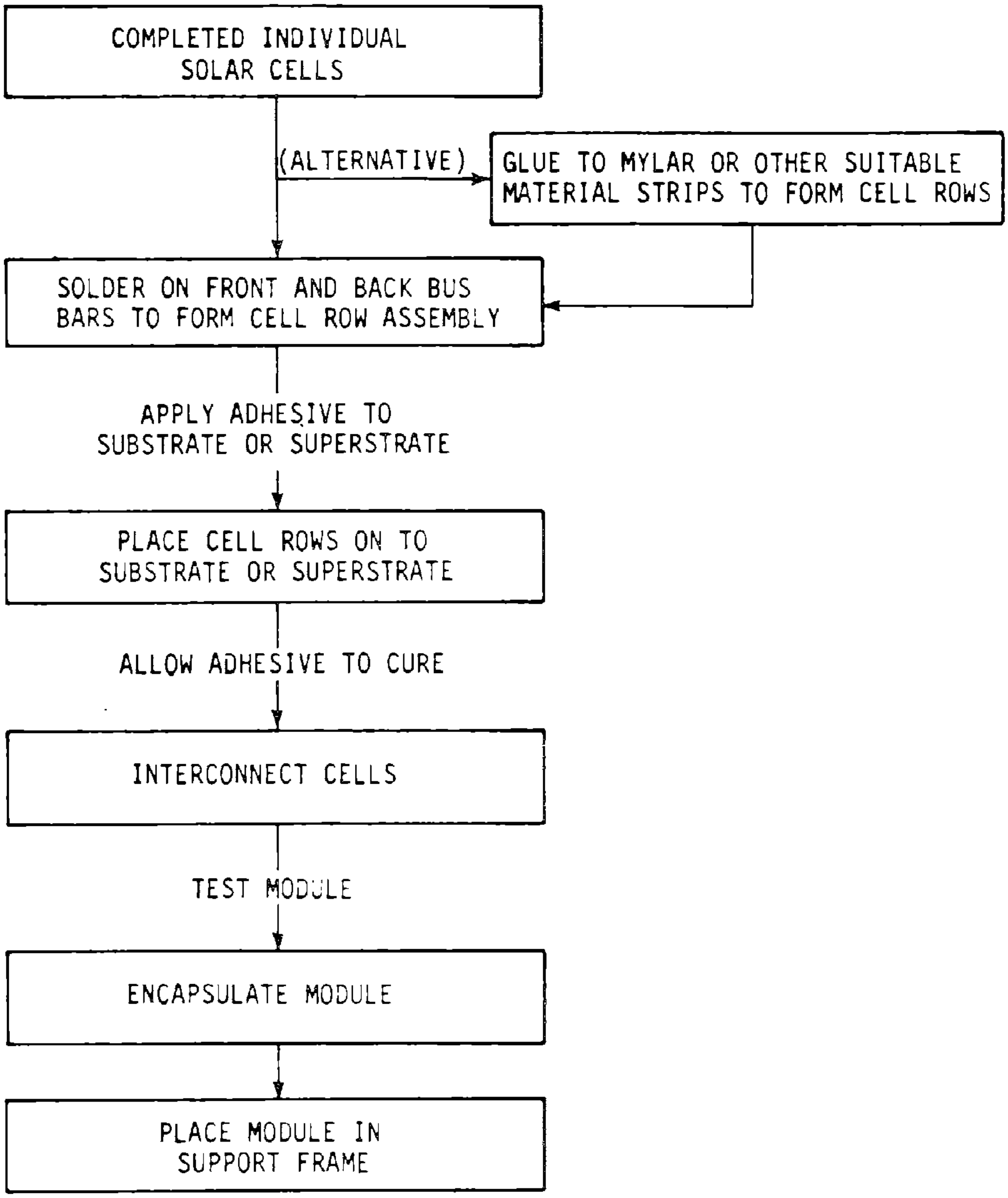


Figure 3-9. Simplified module assembly.

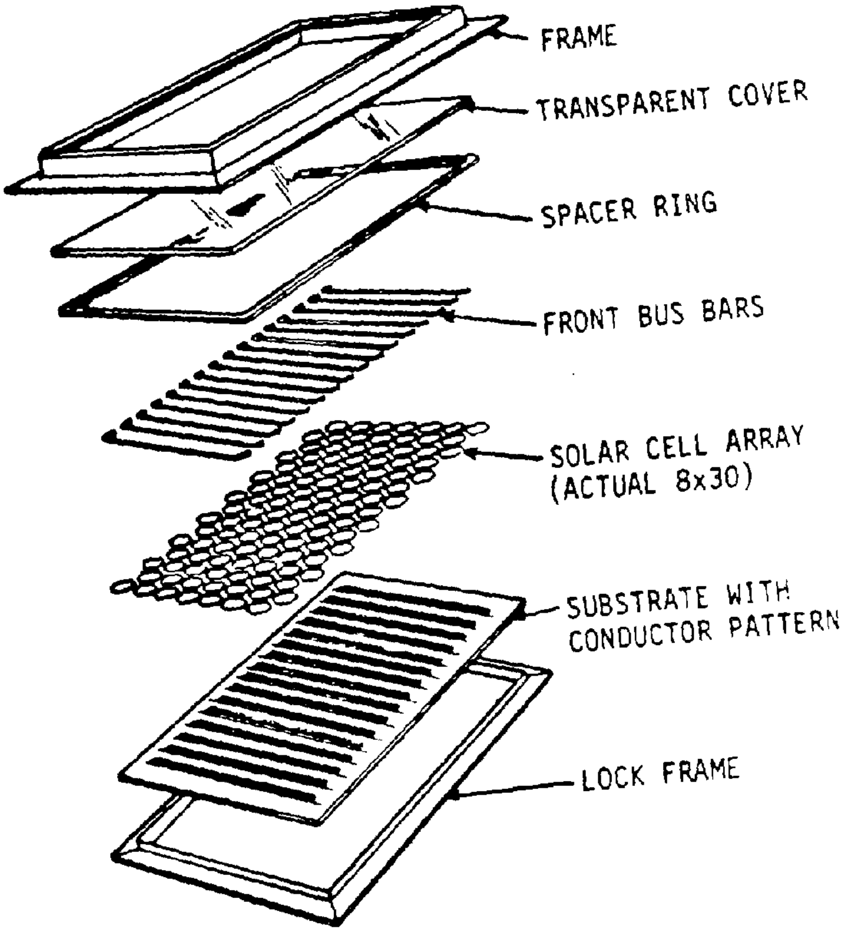
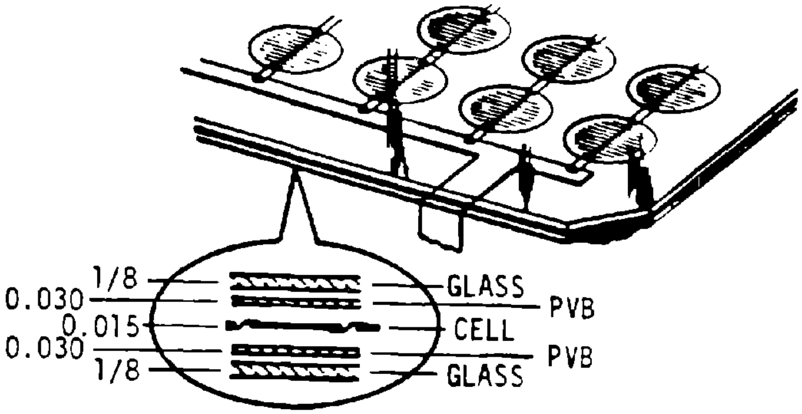
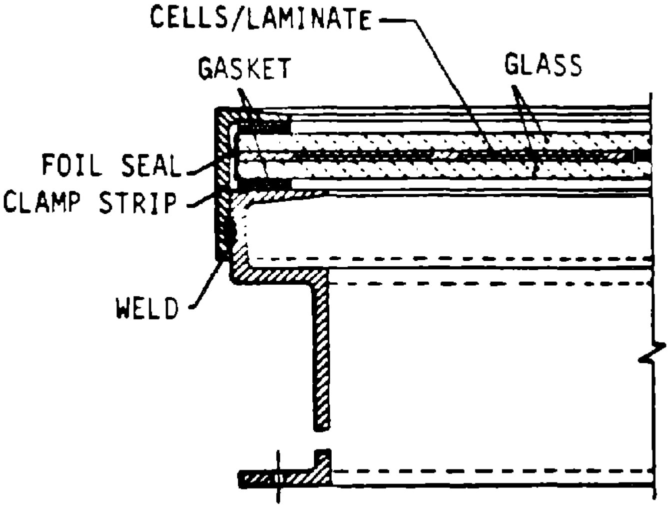


Figure 3-10. Exploded view of proposed LSSA module. (Ref. 25)



a. Three-dimensional and cutaway view of module.



b. Cross section of module and frame.

Figure 3-11. Schematic of proposed module (Ref. 37)

Another method being investigated for interconnection is the use of solder pastes or metallic filled adhesives (28,31). One source considers this a reliable technique (28), whereas another cites the poor electrical conductivities compared with those of metals, questionable performance under thermal and/or mechanical stress, and the high cost of the better solder pastes (gold-filled) (31). These investigators conceded, however, that the technology of metallic filled adhesives is changing and that continuing assessment of new developments is warranted (31).

Ultrasonic soldering, which utilizes ultrasonic energy to smear metal surfaces together, has also been suggested for interconnection (28,31). Because of potential damage to the substrate, however, this is not considered a likely application.

Contact welding, also considered a potentially viable method for connecting the cells (28,31), requires high temperatures and could lead to damage of the cell (31). Further study is needed to determine whether welding can be used. Two other methods of interconnection, thermal compression and clamped connectors, are used elsewhere in the electronics industry but are not considered strong prospects for use in solar cells (31). Interconnect metals proposed for use include copper (26,37), aluminum (37), annealed, expanded silver-mesh ribbon (38), tin-plated copper strips, and solder-coated copper strips (38). One solder consisted of 2 percent silver, 62 percent tin, and 36 percent lead (38). A 60/40 lead/tin solder has also been used, and gold- or silver-filled adhesives may be used (31).

Encapsulation--

The encapsulant materials are also extremely important because they must protect the solar cells against potential damage through a variety of mechanisms including some or all of the following: humidity, air pollution, bird droppings, high winds, salt spray, impact from rocks, hail, sand, rain, snow, handling during cleaning and transport, and vandalism (7). The encapsulant materials should also be resistant to ultraviolet light and must have suitable thermal expansion and thermal dissipation properties, light weight, low cost, and applicability to high-volume production processes (7,31,39). Encapsulation materials can be grouped into three categories: covers; sealants, pottants, or fillers; and adhesives.

The first step in encapsulation involves bonding the cells to the substrate, which usually serves as a back cover, or the superstrate, which usually serves as the front cover. Both substrate and superstrate are the load-bearing components of the module (39). As the name implies, the superstrate rides above the cells and must have high optical transparency in addition to the properties discussed above (39).

In one study the substrates considered were of four basic types: metals, ceramics, plastics, and wood/agricultural materials (39). The superstrates considered were glass and acrylic polymers.

Substrates and superstrates reported in the literature as feasible for module assembly include glass (17,26,28,34,38,40), extruded aluminum alloy (41), aluminum (31), stainless steel (31), cold-rolled steel (31), RTV-615 silicone (41), Rilsan Nylon II-coated steel (31), porcelain-enameled steel (25), Mylar (17,28), Tedlar (17), FEP Teflon (17), Saran (17), and acrylics (17,39). The individual cell or cell string is usually bonded to the sub- or superstrate with an adhesive. Suitable adhesives must provide electrical insulation and thermal conductance.

In the study performed by Springborn Laboratories (39), three categories of adhesives were mentioned for potential use in solar cell applications: solvent-based acrylic adhesives, acrylic latex adhesives, and bulk and hot-melt acrylic adhesives. The bulk adhesives included four types of acrylic adhesives: hot-melt adhesives, cyanoacrylates, first-generation adhesives, and second-generation (or reactive) adhesives (39). Silicone adhesives are also being used for bonding (25), and in one case, polyvinylbutyral (PVB) is used as the glue and filler material (pottant) between two glass plates containing the solar cells (40). Dow Corning Q3-6527 Silicone Dielectric Gel has also been used as a combination filler and glue (38). Other adhesives being used are epoxies (17), FEP Teflon (17), and methyl phenyl types of RTV silicones (17). Several fillers, pottants, or sealants are used to fill in the space between the front and back covers, particularly if glass covers are used. This provides a cushion to minimize transmission of mechanical stress, strain, or shock to the cells and interconnects, and also serves as a glue in some instances to bond the covers together.

Some sealants now being used are Dow Corning Q3-6527 Silicone Dielectric Gel (38), polyvinyl butyrate (28,40), Dow Corning X1-2577 (26), ethyl vinyl acetate (3), and RTV-615 silicone (combination cover and sealant) (41). Other potential sealants identified are polysulfides and acrylic polymers (17). Once the cells are interconnected and sandwiched between the sealant and covers, the unit may be sealed by several methods: (a) by compression at 135°C (275°F) under a moderate vacuum to eliminate trapped air (28); (b) by sealing around the edges with an aluminum foil applied with an acrylic adhesive (40) (see Figure 3-10); or by (c) applying and curing silicon rubber sealer strips on the frame that encloses the module (25). Various hot melt adhesives are also being proposed for use in edge-sealing (28). Table 3-3 lists encapsulation and interconnection materials and methods observed in plant surveys.

TABLE 3-3. MODULE ASSEMBLY METHODS AND MATERIALS AT SURVEYED PLANTS

Plant	Substrate	Encapsulation			Interconnection
		Superstrate	Pottant	Adhesive	
E	Tedlar	Glass	PVB	Edges sealed in hot press. Polysulfide used to seal screw holes	Silver-tin solder paste, set with solder gun
F	Copper-plated panels	Glass	Silicon gel	Silicon gel	Lead-tin solder baths
G	Mylar or fiberglass	Glass or silicon resin	Silicon resin	Silicon resin and Dow sealer	Interconnection tabs soldered with lead/tin
H					
I	Mylar/PVB coating	Glass		PVB	Silver-tin-lead solder baths

3.4 ASSESSMENT OF SILICON SOLAR CELL PRODUCTION

Table 3-4 summarizes information collected during plant surveys. The processes in this table represent essentially the state of the art now used in the photovoltaic industry. Because the industry is relatively new, automation is not yet fully developed and most operations are done on a batch basis. For this reason, cell production is expensive and not yet competitive with conventional sources. The lack of automation is due primarily to the lack of proven technology. The technology is developing rapidly, however, and it is hoped that large-scale plant operation can be realized by 1986.

A number of promising technologies have been developed in each area of the LSA project. Although several approaches within each area are viable, one from each area has been selected for incorporation into a proposed large-scale silicon solar cell production facility (3), called Strawman. This $500/kWp Strawman factory is not a finalized model. Figure 3-12 presents a manufacturing sequence; Figure 3-13 presents a more detailed layout of the plant and the process sequence (3).

The polysilicon process that is proposed by Union Carbide, discussed earlier in more detail. In sheet growth it is proposed that 130 pairs of ribbon-growing machines will be used to produce approximately 30,000 wafers per hour. Each pair of growing machines requires one operator, and each group of ten pairs will have one maintenance man. After the ribbons are scribed and cut, they are placed in cassettes and routed to the cell and module fabrication area.

The wafers are next fed to the back p^+ aluminum spray machines by subconveyors, where they are sprayed with an aluminum powder, fired in an oven on the same machine, and then plasma-etched to remove the oxide (3). From the plasma etchers the wafers are conveyed to ion implant and pulse anneal stations. The conveyor next takes the wafers to the group of metallization machines where a thick-film printing of metal-based ink is applied to the back side, followed by drying in an oven. The wafers are then flipped over, thick-film-printed on the other side, dried, and fired. They are next conveyed to a station for spraying and drying of an AR coating. From the AR coating station they are conveyed to the cell-string assembly area, where industrial robots bond the cells into strips of parallel cells. They go next to an assembly machine, which puts them into fixtures for the vapor-phase solder reflow ovens that follow. Next the cells are evaporated by use of a soda-lime glass sheet for the front, ethylene vinyl acetate (EVA) for the pottant, and Mylar for the back. All interconnections are aluminum.

TABLE 3-4 PROCESSED USED BY SILICON PLANTS SURVEYED

Process	Plant							
	F	D	G	C	B	I	E	H
Single-crystal production	Cz + laser zone crystallization	Modified Cz	None	Cz	Cz zone refining	Cz	Cz	None
Etching and cleaning	Wet[a] + plasma ionization	Wet + mechanical polish	Wet	Wet	Wet + mechanical polish	Wet	Wet	Wet
Junction formation	Diffusion CVD and ion implantation	None	Diffusion CVD	None	None	Diffusion CVD	Diffusion CVD	Diffusion CVD
Metallization	Screen print pattern followed by plating or vacuum evaporation	None	Screen print pattern followed by plating	None	None	Electron beam vaporization	Screen printing	Spin-on screen print followed by vacuum evaporation
Antireflective coating	CVD	None	b	None	None	Electron beam vaporization and vacuum evaporation		Electron beam vaporization
Annealing	Furnace heating	None	b	None	None	Furnace heating	Furnace heating	b

[a] Denotes wet methods.

[b] Insufficient information.

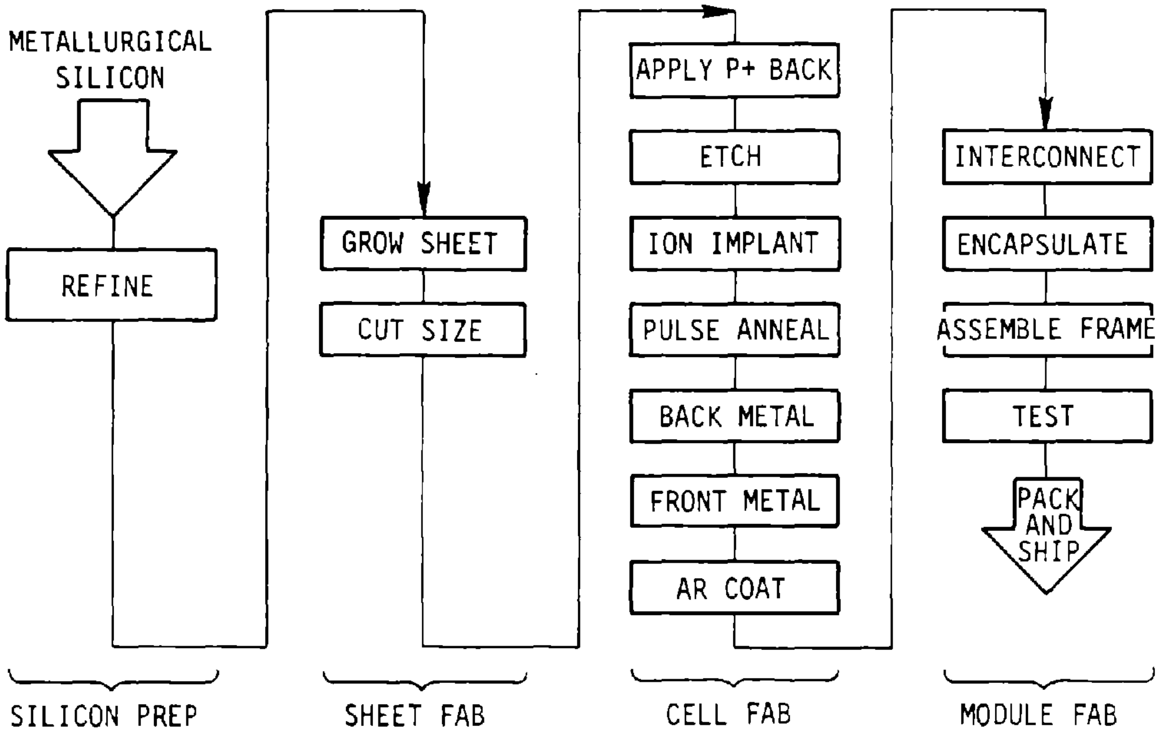


Figure 3-12. $0.05/Watt candidate manufacturing sequence (Ref. 3)

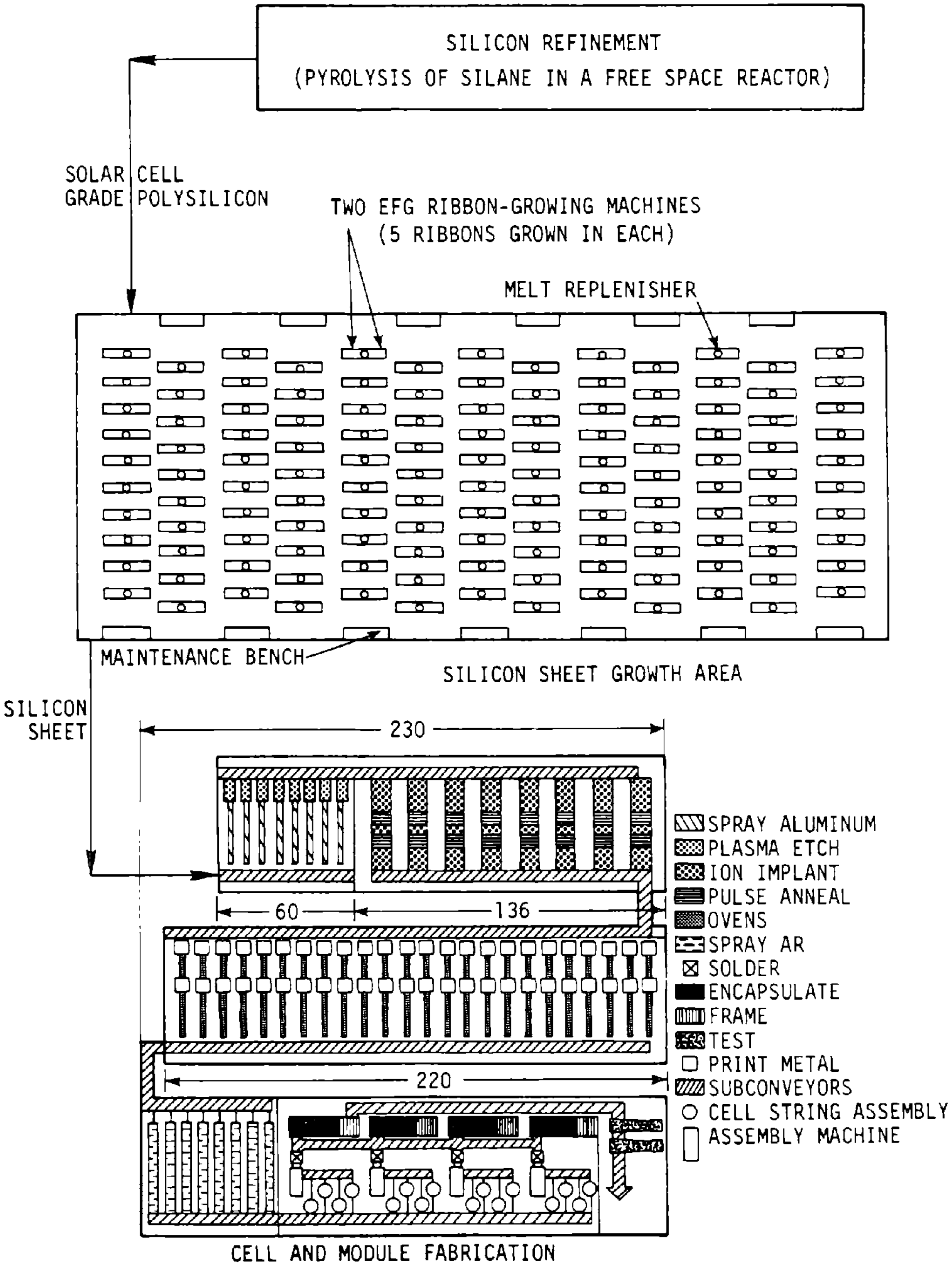


Figure 3-13. Proposed $500/kW$_{pk}$ strawman factory (Ref. 3)

Following encapsulation, the module is framed and connector and terminal wires are hand-soldered. Finally, the 1.2 m (4-ft) panels are tested with a strobe-flash xenon light.

The total personnel requirements for all shifts will be about 1,152 direct workers and 529 indirect workers (i.e., managers, supervisors, etc.). The plant will be able to produce 250 million watts per year, or 160 modules per hour with each module producing 171 watts. The most labor-intensive areas will be the silicon sheet area and the frame assembly area.

From an industrial hygiene standpoint it is important to compare the proposed production plant with those visited as a part of this survey, all of which are either pilot-scale or relatively small in terms of production. Many processes are batch operations requiring much more operator intervention and materials handling than will be needed in the Strawman factory. It is also likely that the proposed plant will require less maintenance and manual cleanup of equipment than the currently used batch equipment. Many of the processes listed in Table 3-4 may eventually become obsolete in silicon solar cell production.

3.5 INDUSTRIAL HYGIENE CONCERNS

This review incorporates survey report data concerning Plants A to I; details are given in the appendix. Individual plants encompass only a part of the total scope of silicon technology discussed here.

3.5.1 Polycrystalline Silicon Production

In production of metallurgical-grade silicon (MG-Si) the primary concern appears to be worker exposure to crystalline SiO_2 and coke dusts. Reduction of quartz in the arc furnace leads to formation of silicon, SiO, and SiC in addition to CO. Low-level exposure to these dusts and the CO gas may occur if the exhaust ventilation system leaks or if it is improperly designed. Replacement or cleaning of filters in the exhaust system exposes workers to the various dusts. Other potential exposure routes are transport of coke and quartz to the arc furnace and milling and conveying of the MG-Si.

Handling of MG-Si in the manufacture of trichlorosilane ($SiHCl_3$) is a potential source of silicon dust exposure. Plant A minimizes fugitive MG-Si dust by using an enclosed conveyor and bucket elevator to transport the raw material from enclosed rail cars to a storage hopper. The conveyor and elevator were vented to a baghouse to collect dust. The chunk MG-Si was then ground to 20 mesh or finer. Grinders were also vented to the baghouse, and all portions of the transport and grinding system were enclosed and/or provided with local exhaust ventilation. Erosion by dust at elbows of the exhaust system has been a problem. Leaks are detected visually and corrected immediately. During a survey of the plant, relatively slight accumulations of silicon dust were observed throughout the building. Somewhat heavy accumulation was noted around the collector box below the baghouse hopper. This reportedly resulted from spillage during changes of the collector box.

Airborne silicon dust constitutes the primary industrial hygiene concern for this area. Personal air sampling reportedly has been conducted, with results generally in the range of 5 to 8 mg/m^3 total dust. Respirable fractions have not been determined. Available health effects data on silicon are extremely scanty. Because this process is highly automated, little operator intervention is required and potential for exposure is minimized.

There is also the potential for exposure of workers to HCl through leaks or accidental releases. At the facility surveyed, HCl comes in rail tank cars or from another process at the facility.

The potential health hazard from HCl is considered to be minimal, with few opportunities for exposure and very limited interaction of personnel with the process equipment. Physical hazards in maintenance and plumbing operations are more significant, and appropriate personal protective equipment is reportedly in use.

The primary industrial hygiene concern throughout the chlorosilane processing and storage areas is exposure to HCl, which would be expected only during maintenance or accidents where the formation of an HCl vapor cloud could occur.

At Plant A these problems were reduced by minimizing the use of pumps and valves and thereby reducing corrosion and maintenance problems. Chlorosilanes are transported by nitrogen pressure. Also, written procedures and employee training are reportedly quite thorough in regard to an HCl "Cloud Alert."

The hazard of hydrogen fire is well recognized at the plant surveyed. It was noted that any hydrogen fire would be visible (smoky) because of chlorosilane contamination of the vent stream. Reportedly, any fire that might occur could be extinguished immediately by nitrogen purge of the vent.

Storage of chlorosilanes before and after fractionation is in pressure vessels equipped with relief devices. Transport of chlorosilanes is entirely by tanker truck. The trucks and loading procedures reportedly meet or exceed DOT requirements. The tank trucks are specially designed with internal shutoff valves. Except for possible HCl exposure resulting from accidental leaks, no significant hazards were noted.

Chlorosilanes production is a fully automated continuous-flow process requiring few operators. Plant A, a major chlorosilane producer, reportedly requires only six part-time operators per shift.

Surveys of plants B, C, and F indicate that the Siemens process, which is the standard technology for production of polycrystalline SeG-Si from trichlorosilane, is well controlled. The feed and recirculation system containing chlorosilanes, HCl, and hydrogen is fully automated. The major routine potential hazards involved bell-jar breakage and open reactors between runs. Feed gas and exit lines are closed in case of bell-jar breakage. Very high exhaust ventilation rates reportedly were used to minimize any emission buildup. Plant B uses a double-wall reactor with a high ventilation rate in the annulus. Also, leaks in the hydrogen system are detected throughout the reactor area by 18 hydrogen detectors, which are set to alarm at 10 percent of the lower explosive limit. Plants C and F use a single-wall reactor and high upflow general ventilation. Plant C reportedly has a 13-second air change rate in the reactor room. Plant F reported periodic reactor glass breakage, which normally results in fire. Because of the high reactor temperature of 1100°C and the presence of HCl, this situation presents a significant hazard potential. The double-wall design used in Plant B should eliminate this hazard.

Sampling conducted at Plant B by PEDCo and Occusafe indicated very low particulate exposure levels in the reactor area. Concentrations ranged from less than 0.02 to 0.11 mg/m^3. No crystalline SiO_2 (less than 1 percent) was detected in the samples. Solvent cleaning of reactor surfaces between runs results in intermittent operator exposure. Plant B used trichloroethylene The high local ventilation rate at the reactor appeared to minimize worker exposure.

Trichlorosilane and hydrogen storage are located outside and away from process areas in Plants B, C, and F. Plant C reported detailed bulk loading safety procedures for these materials.

Overall, the Siemens process appears well controlled and highly automated.

Of the several new processes being developed for low-cost production of SeG-Si, all are highly automated and incorporate continuous flow; thus the manpower needs and interaction of operators and equipment are minimized.

The Union Carbide process as described in the literature (9) for producing SeG-Si from silane is a fully-automated continuous-flow process. The potential hazards should be similar to those of chlorosilane production; however, more processing steps are involved and the hydrogen recycle system and presence of silane require added precautions. Fires due to hydrogen or silane release and chlorosilane leaks of HCl appear to be the main concerns. Hazard detection and fail-safe systems are important design features, together with emergency procedures for operators. No information is available on release of silicon dust or procedures for handling the silicon product as potential exposure concerns. Information on the physical and chemical characteristics of silicon emissions is needed. Also, information on silicon-related health effects is very scanty.

In the new process being developed by SRI (11), the primary industrial hygiene concerns are worker exposures to hydrogen fluoride (HF), fluosilicic acid (H_2SiF_6), silicon tetrafluoride (SiF_4), sodium fluoride (NaF), and silicon sodium fluoride (Na_2SiF_6). Because of the extremely corrosive nature of these chemicals, special precautions should be taken to prevent leaks or accidental discharges into worker-occupied areas. Personnel responsible for cleaning and maintenance should be provided adequate protective clothing. Since cryolite is to be produced as a byproduct, special precautions should be taken during handling and transport to minimize fugitive emissions. Some studies of cryolite workers have shown bone and teeth changes and pulmonary fibrosis (42).

Exposure to fluoride compounds such as silicon difluoride (SiF_2) and silicon tetrafluoride (SiF_4) is also a concern in the process being developed by Motorola.

In the processes of SRI and Westinghouse (12), sodium is used. Maintenance and process personnel should be adequately protected when cleaning, repairing, or replacing parts or equipment used for melting, transporting, and spraying. Precautions should also be taken to reduce the fire hazard of sodium, which ignites spontaneously on exposure to air.

Because these developmental processes are generally highly automated and require little operator intervention, the industrial hygiene problems are minimal. Where potential problems were observed in the surveys, personnel were aware of these problems and system design and operator procedures were being developed to control them.

3.5.2 Crystal Growing and Wafer Slicing

Potential exposure of workers in crystal growing appears to arise primarily from equipment cleaning and maintenance, in which finely divided silicon and its oxides present the major concern. The chemical vapor deposition CVD techniques are potential sources of silane or chlorosilane emissions. Further work is needed to adequately assess the hazards of these processes

Observations at Plants B, C, D, E, F, H, and I, as well as sampling at Plants B and E, indicate that the crystal growing process is of little industrial hygiene concern. At all plants visited this was a very clean process. Results of sampling at Plants B and E for particulate exposures of Czochralski (Cz) operators are summarized below:

Personal Exposures in Cz Processing Areas

	Plant B	Plant E
No. of TWA samples	2	2
Particulate range, TWA, mg/m^3	0.25-0.26	0.13-0.15
Mean exposure, mg/m^3	0.25	0.14
Short-term peak, mg/m^3	0.19	0.16
Bulk sample, total SiO_2, %	12	16
crystalline quartz, %	<1	<1

No high particulate exposures were found. The grower cleaning cycle, which was anticipated to produce the highest exposure, was well contained. No crystalline quartz was detected during the sampling

Sheet and film growth processes do not appear to present significant industrial hygiene problems. Any silicon dopant emissions should be readily controlled with local exhaust. If many units are to be operated in a given work area, care must be given to design of general ventilation to avoid pollutant buildup.

Ingot cropping and grinding is a source of particulate emission, but generally seems well controlled with water lubrication and local ventilation of saws. These operations appeared less controlled at Plant D; similar processes at Plant B with added shielding contained the particulate matter. Four TWA personal samples collected at Plant B for these operations showed particulate exposures between 0.22 and 0.34 mg/m^3. Analyses for crystalline quartz were below the detectable limit (<1 percent). Although particulate levels may be higher at Plant D, it probably does not constitute a hazard.

Cropped ingots are normally etched in strong mixed acids including $HF-HNO_3$ and acetic acid. The ingot etching operation at Plant B was sampled for HF fume. A TWA personal exposure of 0.63 mg/m^3 (0.91 ppm) was found, and a corresponding area sample showed 0.86 mg/m^3 (1.25 ppm). A short-term personal exposure of 3.45 mg/m^3 (5.0 ppm) was also recorded. The etching solution was sprayed on the ingot in an enclosed chamber. At the end of each cycle the chamber was opened to change ingots, and this appeared to cause most of the HF release. The local ventilation was inadequate for this operating phase. Thus, an enclosed hood design is recommended to capture acid fumes. Release of NO_2 is also a concern in this operation.

Multiple-blade/band techniques are also potential sources of oil mist, silicon carbide grit, and clay. If worker exposure in these cutting processes presents a significant problem, control by local ventilation should be effective.

Where laser scribing or annealing is adopted in the industry, numerous hazards may be associated with these operations (43). Atmospheric contamination may arise from several sources:

> Vaporized target material from high-energy laser cutting, drilling, and welding. Materials involved may include asbestos, carbon monoxide, carbon dioxide, ozone, lead, mercury, and other metals.
>
> Gases from flowing-gas lasers or byproducts of laser reactions, such as bromine, chlorine, hydrogen cyanide, and many others.
>
> Gases or vapors from cryogenic coolants.

Among the other hazards of laser operations is ultraviolet radiation, either direct or reflected from flash lamps and continuous wave laser discharge tubes. Ultraviolet radiation is generally of concern only when quartz tubing is used. The ACGIH TLV pamphlet should be consulted for Ultraviolet Radiation exposure guidelines. Glare from high-luminance visible radiation emitted from unshielded pump lamps may lead to chorioretinal injury.

The potential for electrical shock is present in most laser systems. Pulsed lasers utilize capacitor banks for energy storage, and continuous-wave lasers generally have high-voltage dc or RF electrical power supplies. Solid-conductor grounding rods (connected first to a reliable ground) should be used to discharge potentially live circuit points prior to maintenance.

A variety of other potential hazards must be considered. Cryogenic liquids may cause burns; examples are liquid nitrogen, liquid helium, and liquid hydrogen. Operation of some high-power lasers or laser systems involves the potential for explosions at the capacitor banks or optical pump systems. Flying particles may be released from target areas in laser cutting, drilling, and welding operations. Explosive reactions of chemical laser reactants or other gases used in the laser laboratory are of concern in some cases. And finally, potentially hazardous X-radiation may be generated from high-voltage (over 15 kV) power supply tubes.

Plant F is developing a laser remelt process for use with polycrystalline silicon ribbon. All laser chambers have windows designed to adsorb all laser light that might be reflected toward them. Additionally, goggles are worn by all personnel when a laser is on. Warning lights and an automatic lock prevent anyone from entering the process room when a laser is on unless admitted by a technician. This operation appeared well controlled.

3.5.3 Wafer Cleaning and Etching

Cleaning and etching processes are conventionally wet chemical operations performed in hooded enclosed baths. The use of hot concentrated acids such as HF-HNO_3-acetic acid presents a particular hazard because of the high vapor pressure and extremely corrosive action of these substances. The adequacy of ventilation systems is of concern, as well as the technique used for inserting and removing wafer cassettes. At Plant F wet chemical cleaning and etching processes are conducted in "laminar flow" exhaust hoods. Room air is drawn into a plenum at the top of the hood, and supplied to the hood interior by a laminar downdraft. Air is exhausted through a plenum in the bottom of the hood, at flow rates high enough to also ensure a uniform indraft through the front opening of the hood. Hoods are equipped with a static pressure alarm, with an audible signal in the event of fan failure.

At the same plant, safety engineers check the laboratory hoods for proper control velocities and airflow patterns, and affix to the hoods a dated approval sticker.

All exhaust passes through scrubbers prior to venting to the atmosphere, and acid and other waste chemicals are aspirated or diluted with water prior to entering the drain.

Maintenance procedures in wafer cleaning and etching areas must be evaluated carefully. Acute short-term exposure is the major concern. Thus, fail-safe systems in case of equipment failure should be employed. Well-designed ventilation systems should minimize most hazard potential.

Plant D utilizes an automated wafer etching cycle requiring the operator only to remove an etched wafer cassette and replace another unit on a hanger. This is the only time the enclosed hood assembly is opened. In case of a power failure, the room is equipped with emergency lighting and the baths automatically drain. These design features further reduce potential worker exposure.

The wafer etching operators at Plant B, which etches wafers in mixed acids, were sampled for HF and NO_x levels. Etching is performed in several parallel etching booths with laboratory-style hoods. The transfer of cassettes from one solution to the next is performed manually. In analysis of HF exposure at this plant four TWA personal samples ranged from 0.01 to 0.60 mg/m^3 (0.01 to 0.87 ppm) and area samples ranged from 0.01 to <0.01 mg/m^3 (0.01 to 0.02). Analysis of two personal samples for NO_x revealed 0.08 and 0.14 mg/m^3 (0.05 and 0.08 ppm) of NO_2 and 0.10 and 0.17 mg/m^3 (0.08 and 0.14 ppm) of NO, respectively. Two area samples showed similar values. Thus, control appears generally adequate. Ventilation flow measurements taken at the hood face were mainly between 45 and 90 m/min (150 and 300 ft/min). A design shortcoming is the location of the general room supply air close to some of the hoods, resulting in excessive air turbulence near the hood faces. Ventilation rates that are too high tend to cause turbulence and drag out contaminants. An optimum flow rate of about 45 m/min (150 ft/min) should be maintained.

Accidental exposures appear to present the major hazard in these operations. Thus, automation, together with an exhaust fan failure alarm and a fail-safe exhaust system is desirable.

Solvent cleaning areas should have similar ventilation, although side-draw ventilation can be used where relatively nontoxic materials are involved.

Plasma etching and cleaning are vacuum processes that could involve several toxic materials (CF_4 and other fluoride species such as HF, SiF_4). Vacuum pump, exhaust locations, and emissions controls are important considerations. These processes should be fully automated and have relatively lower materials consumption. They may be widely used in the future.

3.5.4 Junction Formation

Although junction formation involves the use of toxic dopants, notably PH_3 and $POCl_3$, the potential for hazard to workers should be low. Safe handling of dopants in hooded areas is essential, together with automatic shutoff of feed lines. At Plant F cylinders for the doping gases, including phosphine, arsine, boron trichloride, and others, are stored inside a ventilated enclosure, equipped with a static pressure alarm that will shut off all gas cylinders in the event of an exhaust fan failure. Plant I uses $POCl_3$ dopant, which is purchased in sealed quartz bubblers. The use of self-sealing fittings reduces potential for leaks in the feed lines. This appears to be a well designed and safe system. Diffusion tube units typically use a side-draw on the tube outlet; if properly designed, this should collect any emissions. Plant G sends the side draw vent gas to a separate water scrubber because of the corrosiveness of this stream.

Ion implantation is a vacuum operation that lends itself to containment of dopant species. A walk-through of one plant showed the ion implantation to be very well controlled. A single operator feeds in the silicon wafers and interacts with the machine only through the control panel. The entire machine is enclosed and vented to the atmosphere. Cylinders of dopant gases are stored in a manner similar to that described above for diffusion.

The major concerns in these processes are adequate handling of dopant gases, automatic emergency shutoff of feed lines, and removal of vented exhaust gas from the workplace.

Polymer dopant techniques should be readily controllable by local ventilation and do not appear to be significant potential hazards.

3.5.5 Metallization and Antireflective Coatings

Metallization techniques, including vacuum plating and printing, appear to present little emission potential. These operations should be readily controllable and of minor industrial hygiene significance. The plant survey showed that metallization is often conducted within laboratory hoods.

Processes involving mask application, electroless plating, and mask removal are potential sources of solvent emissions from the mask and the solvent baths for mask removal as well as plating acid fumes. These sources are all readily controlled by local ventilation.

Several dermatitis and allergic reactions have been noted in the semi-conductor industry in similar work areas. Although none were noted during this study, care must be exercised to prevent skin contact with solvents and to maintain proper ventilation. A glove maintenance program is essential to worker health.

Antireflective coating operations also appear of minor industrial hygiene significance. In design of an exhaust system for chemical vapor deposition with silane and ammonia, the pyrophoric nature of silane must be considered. Wet scrubbing of exhaust gas is a potential control technique.

3.5.6 Module Assembly

Interconnection operations may result in significant emissions from soldering if local ventilation is not provided. Plant E uses small local ventilation devices located on the soldering irons. Measurements of lead exposure from the lead-tin solder revealed levels of 10 $\mu g/m^3$ or less in all samples. Other module assembly operations appear to present primarily physical hazards associated with the many assembly steps.

In general, the number and severity of potential industrial hygiene concerns are reduced by quality control practices requiring clean environments and by efforts to minimize costs by reducing consumption of materials.

Module assembly appears to be the most labor-intensive area, and thus is of importance in this evaluation. Some module encapsulants use epoxy resins, which should be applied and cured under local ventilation. In the production of modules with a silicone resin front surface, plant G sprays a finish coating containing xylene on the surface. This operation is conducted in a bench-level paint spray booth. This appeared to be an adequate design.

3.6 SUMMARY AND RECOMMENDATIONS

1. More information is needed on the toxicity of metallic silicon, silicon monoxide, fused silica, and amorphous silica, all of which may be encountered in the production of single-crystal silicon cells.

2. Toxicological information on silane and the chlorosilanes, including di-, tri-, and tetra-chlorosilanes, is scarce. Because large quantities of these materials are expected to be used, better understanding of potential health effects is needed. Plants producing or using these materials should be equipped with monitors to detect levels of these or associated materials (e.g., HCl) in the workplace. Workers should be advised on emergency procedures and should have access to protective clothing and respiratory apparatus in the event of a large accidental release. Ventilation systems should be fail-safe, with alarms. Also, the extent of decomposition, the decomposition products, and the toxicity of these products should be determined.

3. Very little acute toxicological information is available on several fluoridated compounds that are being used or produced in new processes for polysilicon production. These include fluosilicic acid, silicon tetrafluoride, silicon sodium fluoride, sodium aluminum fluoride (cryolite), and silicon difluoride. Silicon tetrafluoride may also be formed as a byproduct in plasma etching with carbon tetrafluoride. More health effects information is needed on these substances and their decomposition products so that appropriate safety controls and procedures may be determined. It is recommended that areas where these compounds are used or produced be equipped with adequate ventilation systems and alarms.

4. Plasma etching will likely replace wet chemical etching in the future. More toxicity information is needed on carbon tetrafluoride, probably the most widely used plasma gas.

5. More detailed characterizations are needed for some of the dopants used in spin-on junction formation. The exact compositions of these dopants are unknown in most cases. Some of the chemicals reported include tetraethyl orthosilicate, triethyl borate, and pentaethyl phosphate. Toxicological information is needed on these chemicals and on such gases as PF_6 and AsF_6, which may be used in ion implantation or diffusion processes.

6. All acid etching, solvent cleaning, and metal plating baths should have local ventilation in compliance with ACGIH Industrial Ventilation guidelines (178), with fail-safe systems and alarms. Operators should have proper protective clothing, including a face shield, impervious gloves, coat or apron, and armlets. In addition, a program is needed to ensure that gloves are kept clean and puncture free so that workers are not exposed to solvents and allergens. Gloves should be changed at least once a day to prevent outbreaks of dermatitis or allergenic responses.

7. Additional toxicological information is needed on anti-reflective coatings such as tantalum pentoxide and silicon nitride and on spin-on, spray-on, or paint-on antireflective coatings. The compositions of the latter coatings should be determined in more detail. A personal protective program such as that described above is recommended.

8. When interconnection is done manually, the soldering or welding areas should have local ventilation in compliance with ACGIH Industrial Hygiene guidelines (136) to eliminate buildup of toxic metals and other chemicals emitted during these operations.

9. Epoxies used for module assembly and solvents used for cleaning the assembled module can cause dermatitis and sensitization. Adequate local ventilation, good personal hygiene, and protective clothing (as noted above in 6) are recommended.

10. Assembly plants built in the mid 1980's will likely be highly automated, as described in Section 3.3, and will need complex local ventilation systems. Care must be exercised in design of these systems to achieve adequate air flow balance and to provide fail-safe systems and alarms to handle possible accidents.

4. CADMIUM SULFIDE CELLS

Although there is presently no commercial production of cadmium sulfide photovoltaic cells, two companies, Photon-Power Inc., El Paso, Texas, and Solar Energy Systems, (SES) Inc., Newark, Delaware, have proposed commercial-scale operations (4). There are basically two types of cadmium sulfide cells: the back-surface cell, and the front-surface cell. Both of these will be represented in the commercial installations, the back-surface cell using a spray process developed by Photon-Power Inc., and the front-surface cell using a vacuum process developed by SES, Inc.

This discussion of cadmium sulfide cells are primarily focused on the cadmium sulfide/copper sulfide (CdS/Cu_xS) thin-film heterojunction cell, since it is the only one for which commercial production processes have been developed. Brief mention is made of various other semiconductor materials (which are in developmental stages) that are being used in conjunction with CdS.

As an introduction to discussion of cadmium sulfide cell production, the refinement of cadmium and synthesis of cadmium sulfide for use in cell production are considered briefly.

4.1 CADMIUM PRODUCTION

A simplified process flow diagram for production of cadmium from zinc is shown in Figure 4-1. Cadmium has been commercially produced from byproducts of four basic operations, all involving zinc:

1. Fumes and dusts from roasting and sintering of zinc concentrates.
2. Dusts from smelting of lead-zinc or copper-lead-zinc ores.
3. Recycled zinc metal containing cadmium.
4. Purification sludge from electrolytic zinc plants.

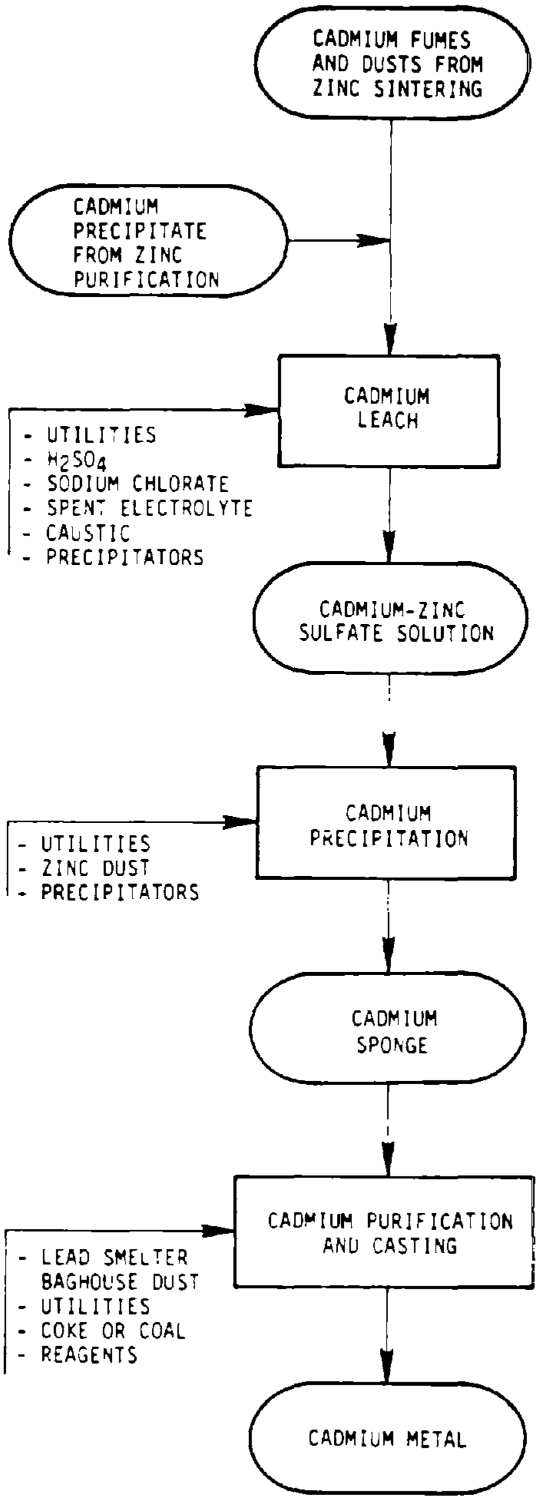


Figure 4-1. Process flow diagram for cadmium production. (Ref. 44)

The first two processes, which are the primary cadmium sources, are discussed below (44).

4.1.1 Cadmium from Zinc Smelter Fumes and Dusts

Various cadmium-bearing dusts, fumes, and sludges from primary zinc plants first undergo a leaching process, which selectively dissolves as much cadmium as possible. Leaching precipitates lead and other impurities without precipitating any of the dissolved cadmium. The fumes and dusts are leached with dilute sulfuric acid and sodium chlorate to ensure complete dissolution of cadmium sulfide. Cadmium goes into solution by the following reaction:

$$CdO + H_2SO_4 \rightarrow CdSO_4 + H_2O$$

Sodium chlorate is a strong oxidizing agent, added to prevent reduction of any sulfur to sulfide and to prevent precipitation of cadmium or thallium as sulfides. Cadmium and lead are converted to sulfates and chlorides. The cadmium compounds remain in solution, but lead is almost completely converted to insoluble lead sulfate.

Instead of a direct leach with sulfuric acid, in at least one plant the dust is first roasted and then water-leached. The sinter fume is heat-treated in a four-hearth roaster, which selectively sulfates the cadmium and makes about 90 percent of it water-soluble. The water leach that follows produces relatively pure cadmium solutions containing about 40 g/liter (0.3 lb/gal) of cadmium and 10 g/liter (0.08 lb/gal) of zinc. Addition of sodium bichromate to this solution removes about 90 percent of the soluble lead. The residual solids are batch-treated with scrubber liquor and concentrated acid.

The cadmium-zinc sulfate solution is then treated with zinc dust to precipitate cadmium as a metallic sponge and then to separate it from most of the zinc dust while the solution is agitated. To avoid excess zinc contamination, usually only 90 to 95 percent of the cadmium in solution is precipitated. The initial precipitation with zinc dust may result in a liquor containing a residual 0.2 g/liter (1.7×10^{-3} lb/gal) of cadmium and 30 to 40 g/liter (0.25 to 0.3 lb/gal) of zinc. To further decrease overall cadmium discharge, the stripped liquor is heated to 40°C (104°F) and precipitated again with 1.6 times the stoichiometric amount of zinc to reduce the liquor to 0.04 g/liter (3.3×10^{-4} lb/gal) of cadmium and 30 to 40 g/liter (0.25 to 0.3 lb/gal) of zinc.

The cadmium sponge (a porous precipitate) is then filter-pressed. It contains about 69 percent cadmium, 30 percent moisture, and small amounts of lead and zinc. It is steam-dried or dewatered in a centrifuge. The solution from filtration, containing practically all of the zinc added and about 10 percent of the cadmium as chlorides and sulfates, is returned to the sintering operation.

The sponge is then processed either by electrolytic or pyrometallurgical methods.

Electrolytic Processing--

In cadmium production at electrolytic plants, the leach liquor is first filtered to remove insoluble copper introduced from the electrolyte. The filtrate is then precipitated with zinc dust in two or three stages to minimize zinc concentration in the cadmium sponge. Strontium carbonate may be added in one of these stages. The sponge will contain about 80 percent cadmium and less than 5 percent zinc. Because the electrolysis step that follows is not highly sensitive to the presence of impurities, the purification step with zinc dust is usually adequate. If further purification is desirable, cobalt may be precipitated with nitroso-2-naphthol or potassium xanthate, and thallium precipitated with potassium chromate or dichromate. The sponge is then oxidized again by steam drying to enhance the solubility of cadmium and is leached in spent electrolyte and filtered. The filtrate contains about 200 g/liter (12.5 lb/ft^3) of cadmium as sulfate and is ready for introduction into the electrolytic cells.

Electrolytic processing of cadmium is carried out in banks of cells similar to zinc cells. The anodes are lead, except when chlorine is present, then irons high in silicon (ferro-silicon) are used. The cadmium cathodes are 97 percent pure and represent 90 to 95 percent total recovery of cadmium from ore to metal. Recovery in the electrolytic step is 96 percent from the cadmium sponge. The stripped cathode metal is washed, dried, and melted under a flux, such as caustic or rosin, and cast into various shapes. Total depletion of cadmium from the solution is not carried out. When the ratio of thallium to cadmium sulfate in the electrolyte reaches 1:10, the cadmium cathodes must be removed and replaced with new insoluble cathodes. Continuing electrolysis deposits an alloy containing 5 to 20 percent thallium. The cathodes are then leached with steam and water to separate thallium into the filtrate, leaving cadmium as a residue. Small amounts of cadmium in solution are precipitated with sodium bicarbonate. Thallium is precipitated with hydrogen sulfide, then dissolved in sulfuric acid. This sulfate solution can be electrolyzed for recovery of pure sponge thallium. The sponge is washed, pressed into blocks, melted, and cast.

Roasting, performed in a Godfrey roaster, causes the cadmium, together with thallium, indium, and selenium, to volatize from the dust charge. The fume is cooled and collected for shipment to a zinc smelter for further processing. The roaster residue, which contains zinc, lead, and antimony, is returned to the sintering machine.

At the zinc smelter, the cadmium dust is mixed with sulfuric acid and water to form a paste, then calcined to a sulfated cake, which is crushed and agitated with spent electrolyte. A lime suspension may be added to neutralize the solution, and sodium sulfide or impure cadmium sulfide is added to precipitate copper and other metal impurities. After filtration to remove a lead cake, an agent such as sodium chlorate is used to oxidize the iron, and lime is used to precipitate iron and arsenic. Heating ensures complete precipitation. Precipitated thallium chromate or dichromate is filtered off after the addition of a soluble chromate or dichromate. Excess chromate remaining may be reduced by sodium sulfide and precipitated by neutralizing with caustic. The filtered solution is fed to the electrolytic plant.

The sponge (a porous precipitate) is first dissolved in dilute sulfuric acid, which has been recycled from another operation. It is then electrolytically processed as described above.

Pyrometallurgical Processing--

In pyrometallurgical processing, the dried cadmium sponge is first mixed with coal or coke and lime. It is then transferred to a conventional horizontal-type retort, where the cadmium is reduced and collected as molted metal in a condenser. Occasionally, to achieve a high degree of purity, the metal is distilled in graphite retorts. Thallium is removed by treatment with zinc ammonium chloride or sodium dichromate. The metal may then be cast into a marketable form or further purified by redistillation. Typical impurities in the product cadmium are 0.01 percent zinc, 0.003 percent copper, 0.015 percent lead, less than 0.001 percent thallium, less than 0.0005 percent tin, and less than 0.001 percent antimony. Cadmium recovery has been reported as 94 percent from the feed to the leach plant and 67 percent from zinc concentrates.

4.1.2 Cadmium from Smelting of Lead Ores

The flue dusts generated by lead smelting are also processed to recover cadmium. Since dust from the blast furnace exhaust gases is recycled to the sintering machine, sinter dust becomes enriched in cadmium, thallium, and zinc.

When cadmium content in the dust reached 12 percent by weight or greater, the dust is subjected to a separate roasting operation for cadmium separation and recovery.

4.2 HIGH-PURITY CADMIUM SULFIDE PRODUCTION

One company reports that the starting material for production of cadmium sulfide is high-purity cadmium oxide (45). The cadmium oxide undergoes reaction with sulfuric acid to produce cadmium sulfate. Alternatively, hydrochloric acid may be used to produce cadmium chloride. In either case the resulting solution is purified by the removal of heavy metal or organic contaminants. Following purification, the solution is gassed with hydrogen sulfide to precipitate cadmium sulfide. The cadmium sulfide that is to be used as photovoltaic material is further purified by high-temperature firing to remove excess sulfate and other volatile contaminants.

4.3 BACK-SURFACE CELL, SPRAY PROCESS

A cross section diagram of a back-surface CdS/Cu_xS cell is shown in Figure 4-2. As the name implies, back-surface (or backwall) cells are illuminated from below through the substrate and CdS layer. Traditionally back-surface cells have been fabricated by the vacuum deposition of CdS on opaque or transparent substrates, followed by ion exchange deposition of a Cu_xS layer. In earlier attempts at back-surface cell construction, opaque substrates of ceramic or copper sheeting were tried. With the use of opaque substrates the Cu_xS layer was first deposited, and then the CdS layer. Cell efficiencies for these types of cells were usually poor (46). Transparent substrates have been used most often in the construction of back-surface cells, and have increased cell efficiency. The forerunner of the basic CdS back-surface cell was fabricated by Carlson and Gorski, first by pyrolytic deposition of an SnO_2 layer onto a glass substrate, followed by vacuum deposition of the CdS layer (46). A Cu_xS layer was then deposited on the CdS surface and contacted with conductive silver paint or a vacuum-deposited silver electrode.

Spray deposition of the CdS and Cu_xS layers was first proposed by Chamberlin and Skarman (47). A diagram of their experimental setup is shown in Figure 4-3. The starting materials that they used for deposition of CdS films are shown in Table 4-1.

TABLE 4-1. STARTING MATERIALS FOR SPRAYED CdS FILMS

Cd	S
Cadmium propionate	Thiourea
Cadmium acetate	N,N, dimethyl thiourea
Cadmium formate	Allythiourea
Cadmium chloride	Thiolacetic acid
Cadmium nitrate	2- thiozoline -2- thiol
	ammonium thiocyanate

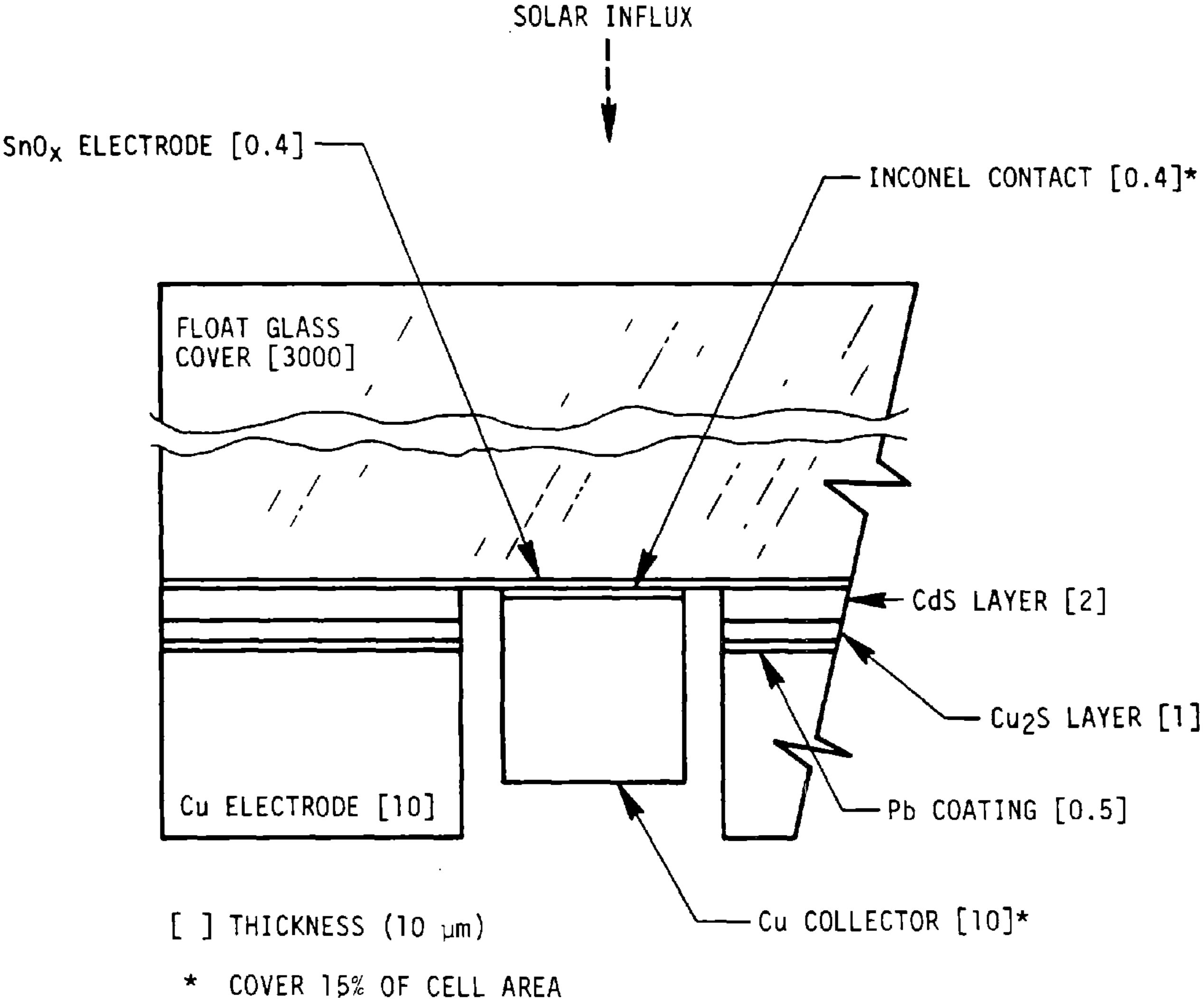


Figure 4-2. Cross section of a back surface CdS cell (Ref. 8)

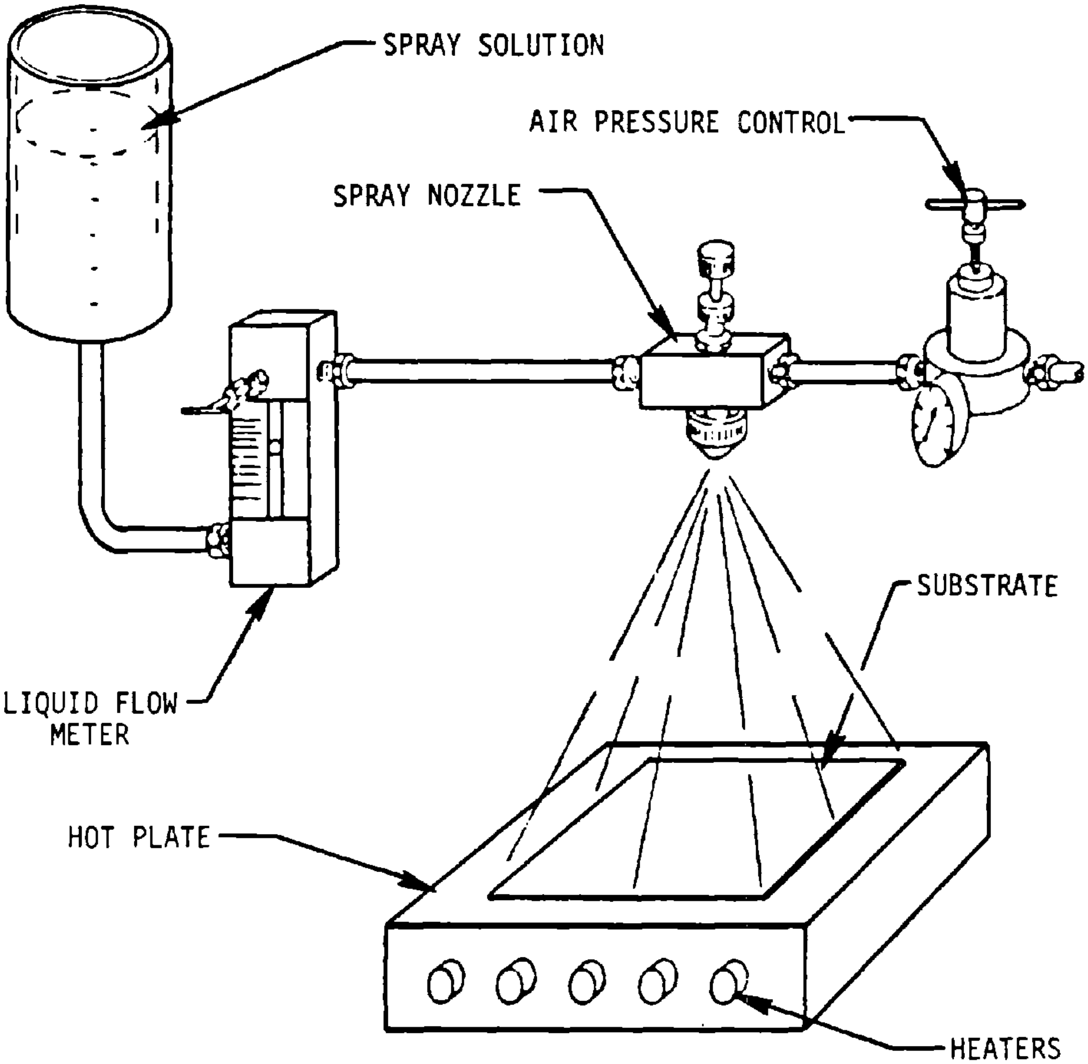


Figure 4-3. Experimental setup for spray deposition of CdS and Cu_xS films (Ref. 47)

According to the authors the semiconductor characteristics of the sprayed film depend on the starting materials, substrate temperature, and crystallinity of the sprayed film. The crystallinity in turn depends on starting materials, substrate composition, and substrate temperature. A heat treatment subsequent to deposition resulted in increased crystallinity without a significant change in crystal orientation.

A high-volume production process using spray deposition for CdS/Cu_xS solar cell fabrication was proposed by Jordon (48). A schematic of this process is shown in Figure 4-4. This is similar to the process that will be used at Plant J, but with a number of significant variations.

At the present time Plant J is adapting the spray process for attachment to a float glass plant. They hope, by 1981, to produce a panel (cell) about 61 cm. (24 in.) square at less than $5/W. This price may be significantly reduced if the spray process can be successfully adapted to the float glass plant. A complete pilot-scale plant is now in operation producing 10 to 20 panels per day. It is hoped that the scaled-up commercial plant can be on-line by June of 1980 and produce 700 to 800 panels per day. The following is a brief description of the pilot process.

The operation starts with sheet glass that is precut or cut to size. The glass is cleaned with detergent and deionized water and then dried in stationary dryers. The plant scaleup will use an automatic washer. Cleaning and drying are important to the production of an adherent surface. Two types of glass are in use: standard float glass and low-iron glass, which allows passage of more light. The glass first passes through a convective furnace, which heats it uniformly to 400° to 500°C (752° to 932°F). When the glass leaves the furnace, a light spray of tin chloride (which oxidizes immediately) in methyl alcohol is uniformly applied to the glass surface. The solution is applied by a spray nozzle, which traverses the glass as it moves steadily along the production line. This is done within an exhaust ventilated enclosure.

The next operation involves a series of seven CdS spray chambers in two groups of three and four each. In the first group, dilute aqueous cadmium chloride and thiourea are applied to form the desired CdS layer of up to 2 μm thickness. The panel then moves to an open area where it is inspected. An operator hand slides the panel to the second battery of sprays, which apply a similar CdS solution to give a total CdS thickness up to 5 μm. The CdS layers are subjected to heat treatment following the sprays. The panel is heated to 450° to 550°C (842° to 1022°F) in an enclosed convective heater. All of these operations take place in ventilated enclosures. The exhaust air from each ventilation system is scrubbed in a separate five-tray countercurrent

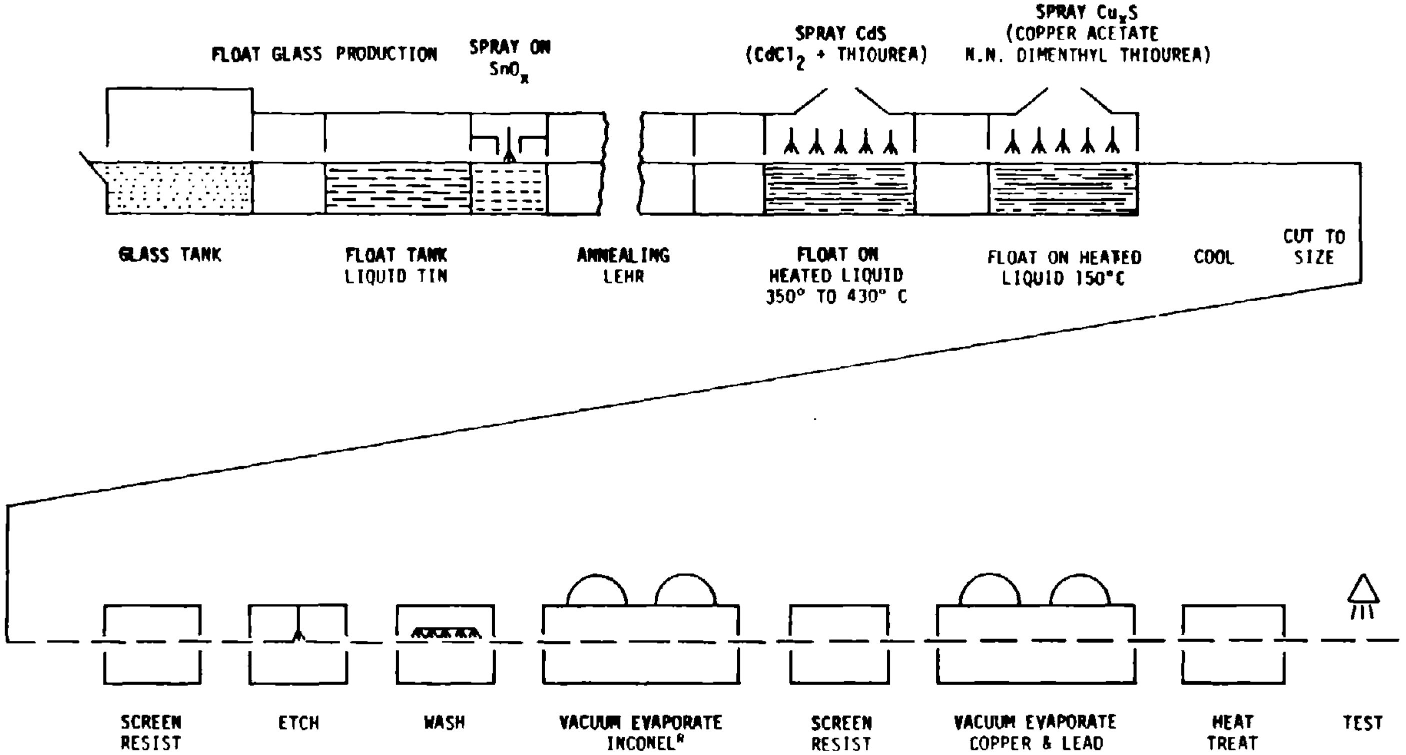


Figure 4-4. CdS solar cell production - back surface cell-spray process (Ref. 48)

water scrubber. Air flow from the scrubbers is exhausted above the roof. Wastewater from the scrubbers goes to two sequential holding tanks. The first tank is baffled to settle solids, and the second is pH-adjusted to precipitate cadmium.

Following the CdS application, the panel is transported to a precision scraping operation where a grid pattern is formed by scraping the lines across the panel down to the tin layer. The tin layer is removed in an arcing operation. A total of 60 lines are scraped sequentially. This operation is automated to produce six lines simultaneously, all indexed. As the lines are scraped, a needle applies a strip of permanent resist while a second applies a removable strip. Compressed air is blown on the panel to remove the dust.

The panel is next placed on a holder and sequentially dipped, by means of a pulley system, into the following solutions to form the copper sulfide (Cu_xS) layer:

1. A pre-edge solution of "mild" tartaric or citric acid.

2. A deionized water rinse.

3. An aqueous solution containing copper ions.

4. A second deionized water rinse.

5. A second aqueous solution containing copper ions of different concentration.

6. A final deionized water rinse.

The copper ion solutions also contain other compounds to form the Cu_2S layer. According to one source the Cu_xS layer can be formed by the chemical spray deposition of copper acetate and N,N,-dimethyl-thiourea (8). It has also been reported that a saturated solution of cuprous chloride (CuCl) is used to form the Cu_xS layer by an ion exchange method (49). The application of the copper acetate and N,N,-dimethylthiourea, or CuCl, results preferably in the replacement of one cadmium atom by two copper atoms, resulting in an interface that retains the sulfur lattice continuity, thus forming the Cu_2S-CdS heterojunction (49). The Cu_2S or chalcocite phase of copper sulfide is preferred because it produces the maximum photovoltaic effect, and thus higher cell efficiencies (50, 51).

The panel, now ready for application of metal contacts, is loaded into a vacuum evaporation chamber that operates at 6.7×10^{-4} Pa (5×10^{-6} Torr). Three metals in pellet form are sequentially evaporated in the chamber as it rotates. After the chamber is broken, groups of panels are unloaded in a slide oven. The oven operates at 150° to 300°C (302°to 572°F), with a circulating air fan. Panels are then cooled, and the temporary removable resistance strip is removed. The panels are now finished and ready for electrical testing and mounting.

The process just described was the pilot-scale operation. Metals used in this operation were considered proprietary, though it was reported elsewhere that Inconel^{R*} (8), or Inconel-aluminum (7) was used. According to one report the Inconel^{R} was used as the negative contact with a negative copper collector, a positive copper electrode, and a positive electrode coating of lead (8). The cells are finally heat-treated at about 260°C (500°F) (8), to obtain higher photosensitivity and better electrical properties (46,52,53,54).

The commercial-size plant will be mainly a scaled-up version of this plant. The spray line will move at about six times the current speed, with about 44 spray booths. About 9,072 kg/yr (20,000 lb/yr) of $CdCl_2$ will be required. Cells produced in this manner have yielded efficiencies of up to 5.3 percent, with average efficiencies in the 4 to 5 percent range (4,8). It is hoped that cell efficiencies of 8 to 10 percent can be achieved when chemical and production problems are solved (8). Problems with the Cu_2S-CdS cell include excess tunneling (passing of electrons through an insulating layer between semiconductors), leakage currents through the interface states, and a poor electron affinity match, resulting in low voltage output (52). To minimize the interface and electron affinity problems, and to increase open-circuit voltage (V_{OC}), the investigators propose replacing the CdS layer with a $Cd_{1-x}Zn_xS$ alloy (55). A potential 15 percent efficiency may be possible with the use of this alloy, but some problems have been encountered. If these problems can be resolved and the zinc-doped cadmium sulfide can be integrated into the spray process, the low efficiency of cadmium sulfide cells may be remedied. Spray application of $Cd_{1-x}Zn_xS$ films has been accomplished in laboratory studies (55). In one study, the $Cd_{1-x}Zn_xS$ solutions were prepared by varying the proportions of $CdCl_2 \cdot 5H_2O$, $ZnCl_2$, and then adding $(NH_2)_2CS$ in a particular ratio, to yield solutions with different mole percent ratios of cadmium to zinc (55). A special hot plate that reaches temperatures up to 500°C (930°F) was used to heat the substrate, and a double-nozzle spray was used to apply the $Cd_{1-x}Zn_xS$ film.

Various other materials are being investigated for use as semiconductors in CdS cells. Recently, a backwall-type cell using CdTe in conjunction with CdS has been developed (7). This cell shows potential for production on a large-scale basis, because it is formed by use of semiconductor pastes and screen printing techniques. A diagram of this cell is shown in Figure 4-5. Cell

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*Inconel^{R}is a trademark of the Huntington Alloy Products Div., International Nickel Co., Inc.

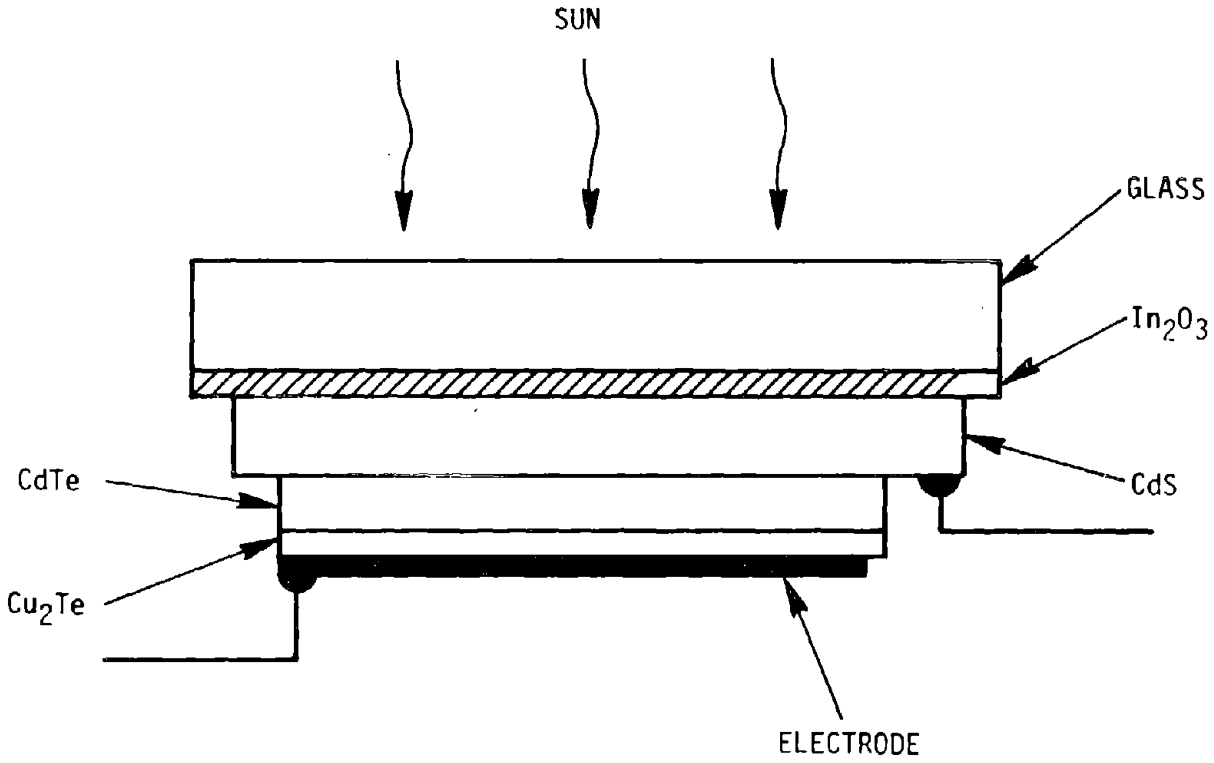

Figure 4-5. Ceramic thin-film CdTe solar cell (Ref. 7)

efficiencies of close to 10 percent (AM2)* have been achieved with this cell.

4.4 FRONT-SURFACE CELL, VACUUM PROCESS

A diagram of a front-surface or frontwall cell is shown in Figure 4-6. The precursor to the modern frontwall cell appears to have been derived by Nadjakov around 1954 (46). The basic frontwall cell consists of a metal (usually molybdenum, copper, or silver), glass, or plastic substrate. If a glass or plastic substrate is used, it must be made to conduct. Silver is usually used as the substrate electrode. A zinc coating may be applied over the silver layer (46). If metal substrates are used, a thin zinc coating is applied to the substrate to reduce the tendency for the CdS layer to form a rectifying contact with them (46). A layer of CdS is next deposited, usually by vacuum evaporation. The more defect-free this film is, the thinner it can be. Deposition of this film may be followed by an etching in HCl (56).

The next layer to be deposited is the Cu_xS. Application of this layer has proved to be troublesome because of the necessity to control the stoichiometry of the reaction so that the chalcocite phase of copper sulfide (Cu_xS) is formed. Besides the spray process discussed above, various other methods have been developed to apply the Cu_2S layer. The first method, referred to as the "wet" method and developed by the Clevite Corp., produces good results (7,50). This involves dipping the cell on which the CdS had been deposited into a 90°C (194°F) aqueous cuprous chloride solution for a few seconds. One solution used for the dipping process consists of deaerated distilled water, potassium chloride (KCl), hydroxylamine hydrochloride (NH_2OH-HCl), hydrochloric acid (HCl), and cuprous chloride (CuCl) (57). The solution used in the Clevite process consists of deaerated distilled water, NaCl, HCl, and $CuCl_2$ (57). A topotaxial ion exchange occurs whereby two copper atoms replace one cadmium atom while the sulfur lattice structure remains the same (50,51). Although various treatments have been devised to help eliminate problems of stability and stoichiometry, it is reportedly still difficult to consistently reproduce the desired cell because of problems in controlling the dipping reaction (7). Efforts to develop other methods of Cu_2S deposition have included use of the "dry" or Phillips process, whereby a dry film of Cu_2Cl_2 is placed on the CdS by evaporation and is subsequently driven in by heat treating at 180°C (356°F) (50). This method involves the same topotaxial substitution as in the "wet" method. Another method involves reactive sputtering of the Cu_2S layer onto the cell by use of an RF diode (51), as shown in Figure 4-7. In RF sputtering a bell jar is evacuated and argon gas is allowed to flow into the system

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*AM2 - Air Mass 2 - Solar spectral irradiance when sun is 60 degrees fron zenith. Air mass is a measure of thickness of the atmosphere between the point of observation and the sun.

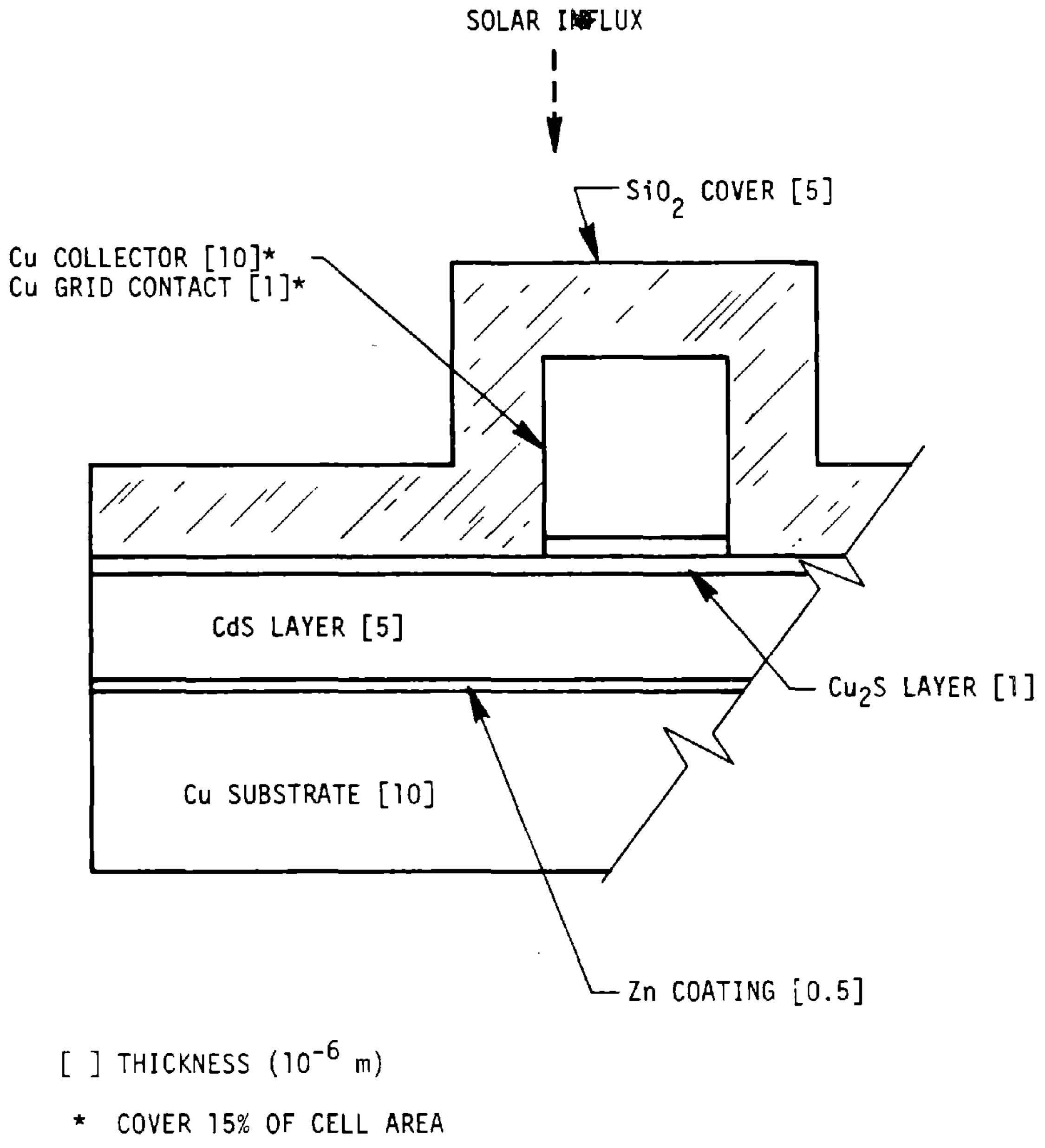


Figure 4-6. Cross section of front-surface CdS cell (Ref. 8)

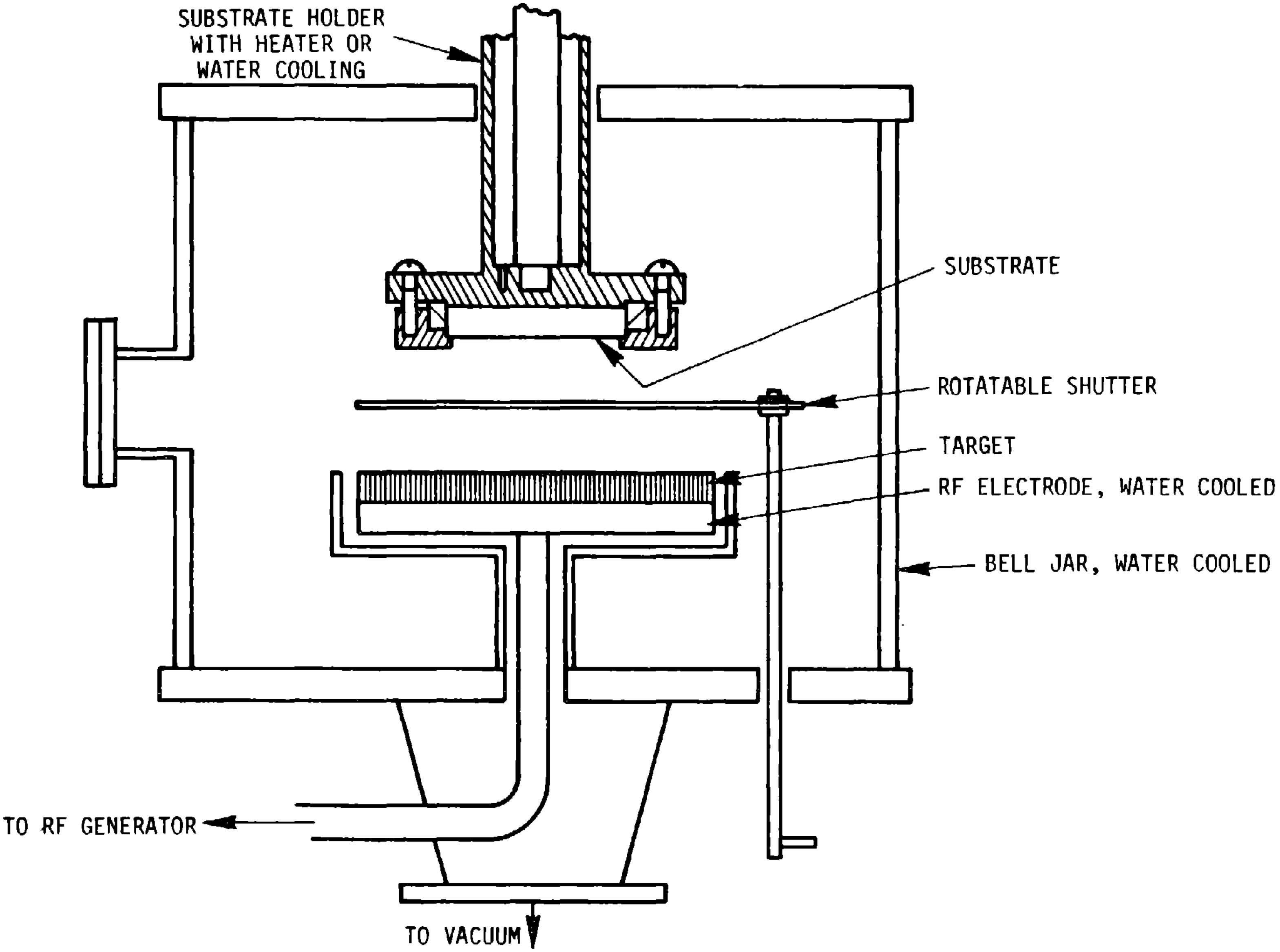


Figure 4-7. Radio frequency sputtering arrangement presently used for semiconductor deposition (Ref. 58)

to maintain a pressure of 6.7 to 13.3 Pa (10^{-1} to 5 x 10^{-2} Torr). The RF generator is adjusted to produce a plasma (charged particles exhibiting good electrical conductivity) disscharge, which excites the argon atoms and causes them to become ionized. The material to be sputtered (target) is bombarded by the argon ions; atoms are discharged from the target material and are propelled towards the substrate to be coated. In this method Cu_xS films are reactively sputtered onto the substrate. Hydrogen sulfide is used as the reactive gas, and the amount of sulfur incorporated into the film is controlled by adjusting the partial pressure of the H_2S.

Another method involves sulfurization of copper in an H_2S-H_2 atmosphere (57). After a thin copper layer has been deposited on the CdS substrate, the sample is allowed to react for 5 hours at 250°C (482°F) in a 1.66 H_2S-H_2 atmosphere and then is rapid-cooled to room temperature. Another method of forming the Cu_xS layer involves sulfurization of copper with thiourea (59).

A metal grid, usually consisting of gold, copper, or silver, is next applied to the Cu_2S barrier layer. The grid may be applied by vacuum evaporation (46,51,60,61,62) or electroplating (46), or a preformed grid may be held in place by covering with a plastic encapsulant (46) or with a conductive adhesive (53). The final step is to encapsulate the cell with a glass or transparent plastic layer.

Two companies have proposed processes for large-scale production of frontwall cells: Plant K and Westinghouse. Plant K will start up a production facility in the near future. Because Plant K is funded privately, information concerning the process is scarce. The following description of the Plant K process is derived from a walk-through survey of the plant and from a discussion by Schock et al. (63) of a similar process.

A diagram of the completed cell developed by Schock et al. is shown in Figure 4-8. A silver layer and then a CdS layer are first deposited on ordinary window glass by vacuum evaporation. The silver layer serves as the contact and is 0.5 μm (2 x 10^{-5} in.) thick. A schematic of the apparatus used for vacuum evaporation of CdS is shown in Figure 4-9. Deposition of the CdS is controlled by controlling the shutter, the temperatures of the substrate and the source, and the pressures of the gases within the chamber. The rate of deposition is 1.5 μm (5.9 x 10^{-5} in.) per minute, and the final thickness of the CdS layer is 30 μm (1.2 x 10^{-3} in.). The substrate temperature is kept at 180°C (356°F). A pilot plant producing these cells operates three of these CdS vacuum evaporation units simultaneously.

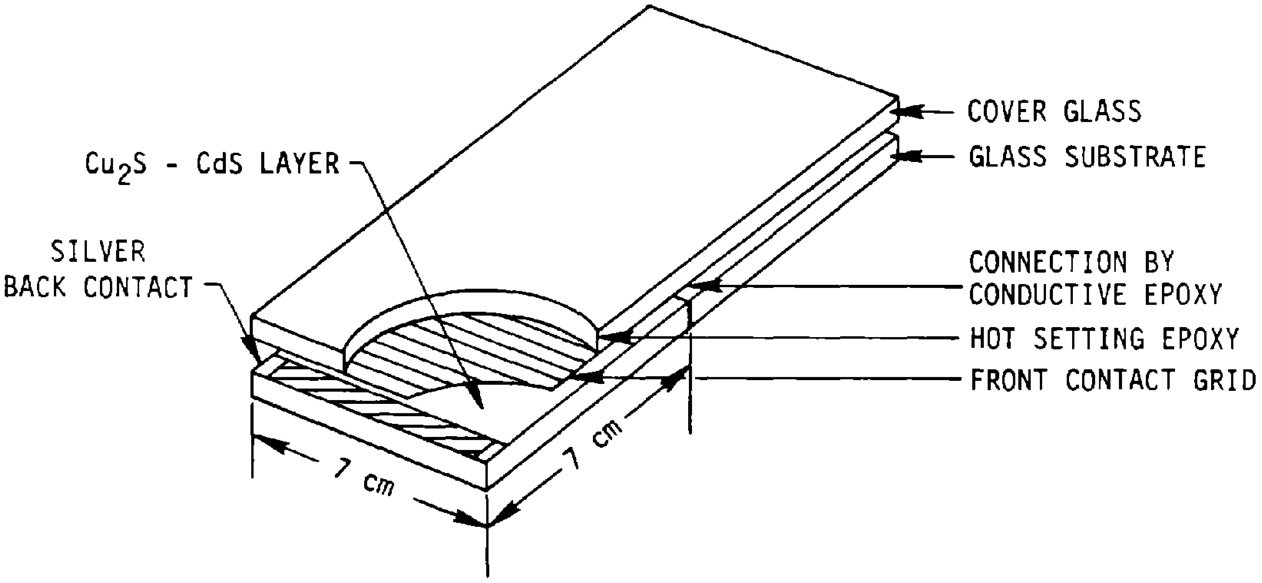


Figure 4-8. Structure of a Cu_2S-CdS thin-film solar cell module (Ref. 53)

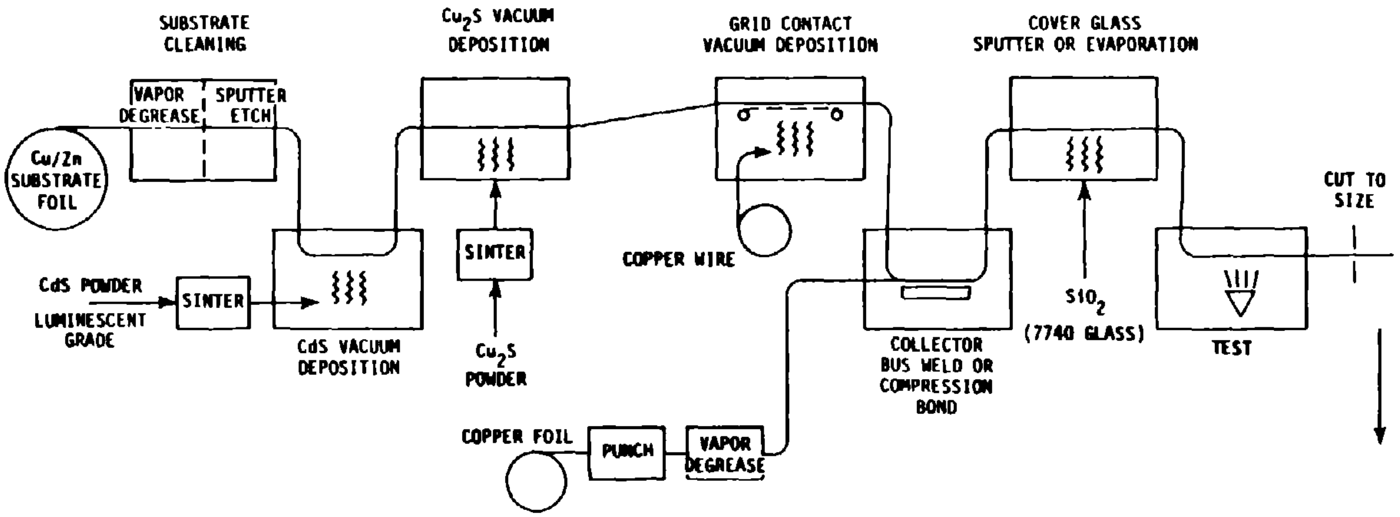


Figure 4-9. CdS solar cell production - front surface cell-vacuum process. (Ref. 8)

In the Plant K process rolled steel cut to approximately 20-cm (8-in.) squares is used as the substrate. First the steel substrate on the leaf holders is cleaned in a degreasing bath containing Freon. The substrate is then prepared for the back contact and thin bonding layer applications by sequentially dipping the substrate in an alkali cleaner, a dilute sulfuric acid solution, and the back contact solution, followed by a spray rinse.

A large horizontal vacuum evaporator is then used to evaporate the CdS under controlled temperature and pressure to produce the desired crystalline CdS coating on the steel plates. The batch operating cycle, which requires several hours, includes loading the substrate (in individual holders), closing the vessel end flange, pulling a vacuum, operating heating and cooling cycles, evaporating the CdS powder in crucibles, and releasing the vacuum. A roughing vacuum oil-sealed pump located adjacent to the evaporator is vented to the outside. The vessel is equipped with cryogenic shields to reduce the amount of CdS vapor leaving the vessel.

Plant K is designing a semicontinuous evaporator equipped with air locks to prevent exposing the hot chamber, which can then operate without being opened.

In the process of Schock et al. (first process described above), the cell after deposition of the CdS layer is etched in a 1:1 solution of HCl and water at 60°C (140°F). This causes formation of pyramidal tips on the columnar CdS grains and increases light absorption of the final cell.

In the Plant K process deposition of the CdS is followed first by application of an impervious compound. This operation is performed piecemeal under a small hood. The substrate, held on a carrier, is then dipped into a strong acid solution, followed by a rinse bath.

In both processes the cells are dipped into copper solutions following the acid etch. The solution in the Plant K process is described only as a copper salt, whereas in the process described by Schock et al. it is a CuCl solution, maintained at pH 5. This results in the formation of the Cu_xS layer.

The next step is application of contact grids. In the Plant K process contact grids consisting of copper, nickel, and gold layers are applied sequentially by a proprietary process and laminated. Local ventilation is used in each application stage. The cells are then encapsulated in a metal pan with a glass cover and hermetically sealed to exclude oxygen and moisture. In the process of Schock et al. a thin layer of copper is deposited over the Cu_xS-CdS layer to improve the efficiency and stability of the cell. In a separate step the grid structure, which is a screen-printed, etched copper foil 35 μm (1.4 x 10^{-3} in.) thick, is stuck to the cover glass with a hot setting adhesive. The grid is also plated with a thin gold layer to provide optimum contact. The top half of the cover glass and grid is then joined to the bottom half by means of the hot setting adhesive. Four of these single cells, which are 7 by 7 cm (2.8 by 2.8 in.), are then sealed in a press that uses a conductive epoxy to join the individual cells together. Although most of the cells produced in the pilot production unit have shown efficiencies of 3.5 to 4.0 percent, the range has been from about 0.5 to 5.5 percent, an indication of difficulties with cell reproducibility (53).

A process diagram of the operation proposed by Westinghouse is presented in Figure 4-9. A cross section of the finished cell is shown in Figure 4-2. Deposition of the zinc, the CdS, the Cu_2S, the copper grid, the copper collector bus, and the final SiO_2 (quartz) cover onto the copper foil substrate occurs within a large vacuum chamber. The only operations that take place outside of the vacuum chamber are degreasing of the substrate and grid material (8). Although it is reported that efficiencies of up to 8.6 percent have been measured for cells produced in this manner, the efficiencies of cells produced on a pilot scale typically have ranged from 2 to 3 percent (4).

4.5 ALTERNATIVE SEMICONDUCTOR MATERIALS FOR USE IN CADMIUM SULFIDE CELLS

Other semiconductor materials being investigated for use in CdS backwall cells are indium phosphide (InP) (7,52), copper indium selenide ($CuInSe_2$) (7,52,57), and copper indium sulfide ($CuInS_2$) (7,57). Heterojunctions based on single-crystal substrates of CdS/InP and CdS/$CuInSe_2$ have shown efficiencies of 15 and 12 percent, respectively, whereas thin-film cells of CdS/InP, CdS/$CuInSe_2$, and CdS/$CuInS_2$ have yielded cell efficiencies of 5.7 (AM2), 6.2 (AM1), and 2.9 percent, respectively (7). It is significant that the CdS/$CuInSe_2$ cell is one of the few cells (along with CdS/Cu_2S, amorphous Si, and GaAs thin-film) with efficiencies above 6 percent (58) that can be produced by a potentially inexpensive means. Figures 4-10 and 4-11 illustrate a CdS/$CuInSe_2$ cell and a proposed automated production process, respectively (58). Of course the development of sputtering techniques for thin-film applications could provide a potentially inexpensive means for depositing various heterojunction combinations. Data obtained with existing partially automated systems indicate that 10 percent efficient solar cell subpanels can be fabricated in a system similar to that in Figure 4-11 at an estimated cost of \$0.15 to \$0.50 per peak watt (58).

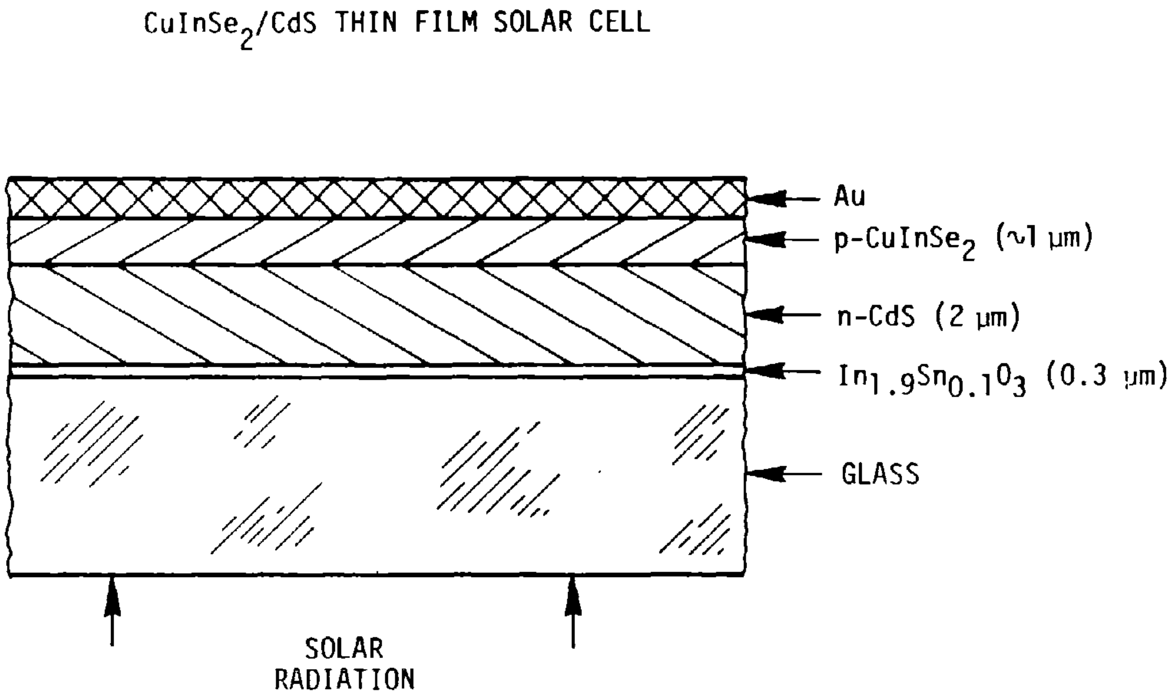
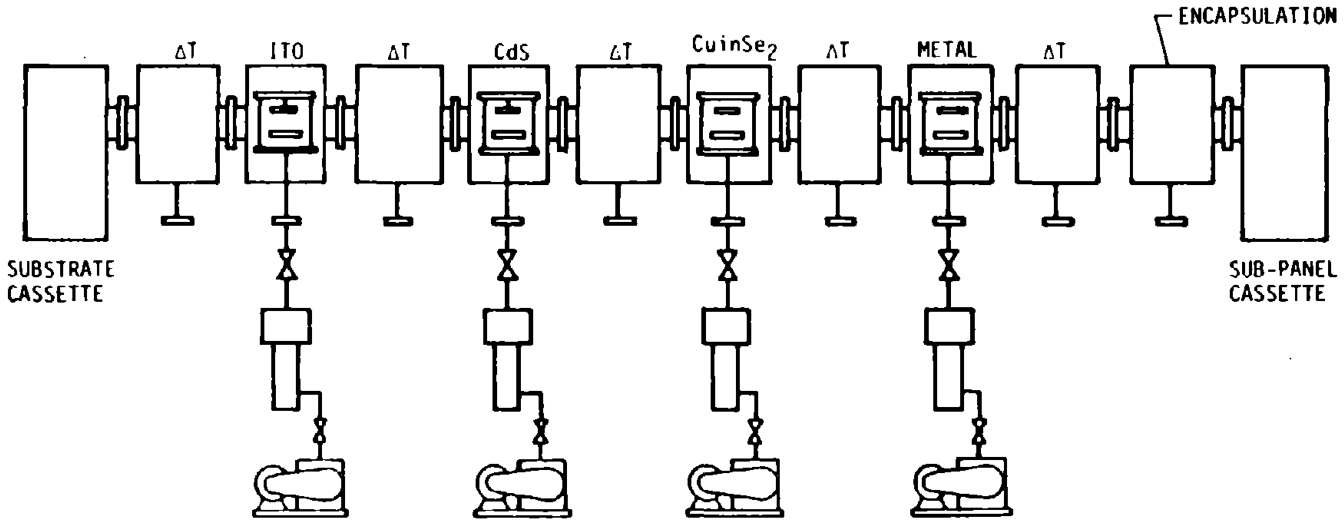


Figure 4-10. Structure and dimensions of proposed "backwall" thin-film solar cell (Ref. 58)



AUTOMATED SEQUENTIAL SPUTTER DEPOSITION SYSTEM

Figure 4-11. Automated sputter deposition system for fabrication of encapsulated arrays of metal/$CuInSe_2$/CdS/ITO solar cells on glass sheets (Ref. 58)

A number of mixed I-III-VI (valence) compounds are being investigated for use as semiconductors with cadmium sulfide. Besides $CuInS_2$ and $CuInSe_2$, already mentioned, silver indium selenide ($AgInSe_2$), copper gallium sulfide ($CuGaS_2$), and copper gallium telluride ($CuGaTe_2$) have been investigated. Also, some pentenary materials have been synthesized (63). These include about 20 variations of $Cu_xAg_{1-x}InSe_{2}S_{2(1-y)}$ and $CuAl_yGa_{(1-y)}Se_{2(1-z)}Te_{2z}$. The desired end in synthesizing these various materials is to obtain a suitable semiconductor material with a lattice constant identical to that of CdS and an energy gap optimum for solar energy conversion, which would be approximately 1.5 eV (57).

4.6 INDUSTRIAL HYGIENE CONCERNS

The primary concern in the production of CdS solar cells is the potential for worker exposure to cadmium vapors, fumes, or dusts that may enter the work environment from spray or vacuum processes. In addition to cadmium levels, the levels of metals, solvents, etchants, resists, and other materials should be determined so that exposure of workers can be controlled by altering the system design, by effective ventilation, or by implementing the appropriate work practices, industrial hygiene practices, and control measures. In addition to the need to determine concentrations of the various chemicals used, more toxicological information on some of these is needed. Several processes utilize chemicals or metals that are proprietary. Although it is a company's right to preserve the uniqueness of a process, it is also their responsibility to see that appropriate measures are taken to protect those who work with potentially hazardous chemicals.

The following sections concern specific problems related to the CdS/Cu_2S cell production facilities surveyed in this study. Application of the Cu_xS layer is not discussed because this process step did not appear significant in the survey. Other methods of deposition with potential application to commercial production are spray deposition, reactive sputtering, and sulfurization of copper films. Ion exchange by dipping is currently used in both back-surface spray and front-surface vacuum processes. Spray deposition may cause emissions of organic or chlorinated copper compounds and sulfur compounds such as thiourea and N,N,-dimethylthiourea. Reactive sputtering and sulfurization may involve the use of toxic gases, such as H_2S, under pressure.

4.6.1 Back-Surface Cell, Spray Process

The primary concern in this process is potential exposure to airborne compounds applied by spray deposition. These include CdS, cadmium chloride, tin compounds, thiourea, and methanol.

In a recent survey of Plant K, a CdS cell pilot plant, area samples and personal samples were collected for analysis of cadmium and lead dust and fumes, and personal samples were taken for lead, thiourea, methyl alcohol, toluene, and tin as tin oxide. Table 4-2 summarizes results of the sampling survey. All samples were analyzed according to NIOSH procedures.

The following conclusions are drawn from this survey:

1. Most time-weighted average personal exposures to cadmium were below 30 $\mu g/m^3$ and were below the OSHA standard for cadmium fume of 100 $\mu g/m^3$. No apparent reason was found for the two elevated exposures (59.3 and 58.5 $\mu g/m^3$).

2. Area samples showed low cadmium levels.

3. Elevated exposures were, apparently, due to insufficient spray chamber ventilation and local ventilation or to reintrainment of cadmium dust.

4. Care should be exercised in personal hygiene to avoid ingestion of cadmium. Operators were observed handling contaminated equipment with bare hands. Also, workers wore contaminated work clothes when leaving the workplace. These practices should be changed.

5. Some elevated cadmium exposures occurred during cleanup operations. Until cadmium exposures are reduced in these operations, each worker should wear a fitted mask with air-purifying cartridge.

6. Workers should exercise care when handling waste sludges, and cleaning settling tanks.

7. Exposure to thiourea was comparable to cadmium exposure levels. Although no TLV has been set for thiourea, it is known to be highly toxic. Available toxicity data on thiourea should be reviewed and an interim TLV set. Then if the exposure level exceeds this interim TLV, the level should be reduced. The American Industrial Hygiene Association, Committee on Workplace Environmental Exposure Levels can be consulted to develop such interim TLV's.

8. Improved cleanup procedures and/or improved ventilation during cleanup should be implemented.

9. There is a potential hazard from emission of ultraviolet radiation during the arcing operation in cell subdivision.

TABLE 4-2. SUMMARY OF PILOT PLANT SAMPLING SURVEY

Sample description	Location	Operation	Substance sampled	Concentration range, μg/m^3	Estimated TWA Range, μg/m^3
	PERSONAL SAMPLES				
Cd_2S spray operators	Spray line	Normal Cleanup	Cadmium	13.8-28.2 15.6-821	16.4-506
Tin oxide spray operator	Spray line	Normal Cleanup [b]	Cadmium	18.9-29.8 11.9-48.7	21.4-38.5
Supervisor	Throughout plant	Not applicable	Cadmium	9.8-58.5 4.4-6.0	5.5
Tin oxide spray operator	Spray line	Normal Cleanup	Tin	5.5-19.7 28.9-45.3	9.0
Supervisor	Throughout plant	Not applicable	Tin	0.5	
Operator	Spray line	Preparation of Cd_2S No. 1 spray solution Cleanup	Thiourea	44.5 22.8	30.8
Cd_2S spray operators	Spray line	Normal	Thiourea	3.0-21.2	20.8
Cell division operator	Cell division	Primarily cleanup	Cadmium	65.7	
Cell division operator	Cell division	Cell division and cleanup	Cadmium	5.6	
Cell division operator	Cell division	Preparation of lead bullets	Lead	5.0-17.1	
Cell division operator	Cell division	Cleaning permanent resist lines	Toluene		
Chemist	Spray line	Sampling exhaust from spray line area	Cadmium	26.9	
	AREA SAMPLES				
Area	Between Cd_2S spray lines		Cadmium	12.9	
Area	Spray area over glass dumpster		Cadmium	9.0	
Area	Outside workshop about 46 cm from vacuum blower discharge		Cadmium	9.8	
Area	Same as above		Cadmium	14.8	
Area	Downwind about 1.8 meters from Cd_2S spray exhausts		Cadmium	80.1	

[a] Ranges are given only where two or more samples were taken.

[b] After finishing cleanup of their equipment, tin-oxide spray operators helped clean Cd_2S spray equipment.

10. In general the work areas are well controlled considering that this is a pilot line facility. A full-scale operation would be more continuous, and thus more complete enclosure of operations would be needed.

4.6.2 Front-Surface Cell, Vacuum Process

Because many of the operations observed on the survey are performed batchwise and intermittently, the value of the industrial hygiene review is limited.

The major potential for exposure to CdS appears to occur when dust is released during handling and weighing prior to evaporation, when the worker contacts CdS-coated surfaces while unloading and loading substrate in the evaporator, and when the CdS coating is removed from the evaporator inner walls. The latter operation appears to have the highest exposure potential; the maintenance operation would be required periodically even with a continuously operating evaporator. During vacuum deposition the system is under a negative pressure gradient, and leaks into the workplace air are not likely unless the vessel is damaged or a malfunction occurs. Leaks from pump seals, system plumbing, and similar components are other possible sources of exposure.

Although no significant industrial hygiene problems were observed at Plant L, many operations cannot be adequately characterized because of the proprietary nature of the process and the bench-scale level of the process operations. In addition, some phases of the process were not in operation during the survey.

On the basis of observations and available information, there are several areas that require further consideration. To prevent the potential contamination of a large area the CdS evaporation vacuum pumps should be isolated in a separate room and should be vented to the atmosphere. One critical area for worker exposure is during cleanup of CdS buildup from the evaporator inner wall. This procedure should be studied and revised to avoid work entry. In the interim period workers performing this function should be monitored for air exposure to CdS dust. Although Freon is relatively nontoxic, the base-plate Freon degreaser should have local ventilation in keeping with good design practics.

4.7 SUMMARY AND RECOMMENDATIONS

1. With respect to control of cadmium vapors, dusts, and fumes, the areas requiring special attention include raw materials handling, materials preparation (i.e., solution mixing and weighing of materials), spraying, and maintenance of equipment.

2. Ventilation systems for cadmium spray chambers, vacuum chambers (for cadmium application), thiourea spray stations, lime scraping stations, acid etching tanks, metal plating tanks, and solvent cleaning tanks should incorporate a fail-safe design with automatic shut-off and/or backup ventilation systems. Vacuum pumps handling toxic materials should be isolated or a fail-safe design should be used.

3. In a full-scale production facility, critical areas should be monitored routinely for cadmium to ensure the maintenance of safe levels. Potential for exposure of workers to cadmium appears highest during cleaning and maintenance operations in cadmium processing areas. Engineering control emphasis should be placed on these processing operations.

4. Little toxicological information is available on thiourea or N,N,-dimethylthiourea. In a sampling survey, thiourea levels were comparable to cadmium levels. Further study is needed to determine the potential acute and especially chronic effects of these compounds.

5. GALLIUM ARSENIDE PHOTOVOLTAIC CELLS

In an effort to enhance cell performance, high-efficiency cells have been devised for use in conjunction with sunlight concentrator systems. Because they have a small absorber area, these cells can be manufactured at a lower cost per watt, with the savings going toward purchase of other system components. Also, with concentrator systems higher conversion efficiencies are possible than with flat-plate systems, and less land is needed for a system of the same output.

Two major types of concentrator cells, silicon and gallium arsenide, are being developed. The gallium arsenide concentrator cell is discussed here. Fabrication of gallium arsenide cells is currently done with laboratory equipment. Gallium arsenide is attractive for use in concentrator cells fabrication for several reasons. First, it possesses an optimum bandgap, along with other properties for high photovoltaic conversion efficiency (52,64,65). Also, a gallium arsenide cell maintains its efficiencies far better at high temperature than does a silicon concentrator cell (52,64,65). The high temperature tolerance of GaAs cells makes them attractive for use in hybrid systems using thermal as well as electrical energy (52). A major disadvantage of GaAs cells at the present time is the high cost of production, which may be as much as an order of magnitude higher than the cost of silicon cells (52,66). Another potential problem with GaAs solar cells is the availability of gallium. It is estimated that the domestic gallium reserves are approximately 15 Mg (16 tons) in bauxite ores, but that a significant quantity is also available in zinc ores (67). It is estimated, however, that in the year 2000 alone, some 32 Mg (35 tons) of gallium will be required for purposes other than solar cells (8). An additional 0.3 Gg (2533 tons) would be required if 4500 MW of GaAs solar cells were to be produced (8). Thus supplying the gallium for solar cells alone would require an order-of-magnitude increase in production over that needed for purposes other than solar cells. Gallium is primarily a byproduct of aluminum refining, and the feasibility of increasing aluminum and/or zinc production to meet the increased demand for gallium is low. It is possible, however, that the use of concentrator systems with solar concentration capacity of at least 100:1 and reduction in cell thickness of the single-crystal cells could reduce the gallium demand to less than 2 percent of that which is currently projected (8). Most GaAs cells will be designed for concentrations several times greater than 100:1.

The following discussion includes process descriptions for production of gallium and arsenic, as well as fabrication of GaAs photovoltaic cells.

5.1 PRODUCTION OF GALLIUM

Although it is predicted that zinc refining will also become a source of gallium, aluminum ores (bauxite) are presently the main source. Figure 5-1 is a process flow diagram for extraction of gallium from bauxite.

In the extraction of sodium aluminate from bauxite, caustic is used. From this caustic solution the aluminate is precipitated by bubbling CO_2 through the solution. The caustic solution is recirculated and reused for extraction of aluminate from bauxite. Eventually the recirculation of the caustic solution results in a buildup of gallium. After the ratio of aluminum to gallium in the caustic solution reaches approximately 500:1, the aluminate is precipitated with CO_2. The filtrate is then treated with additional CO_2 to precipitate the gallate and remaining aluminate. The precipitate is subjected to a leaching with sodium hydroxide to yield a gallate-rich leachate, from which the gallium is electrolytically deposited. The gallium is 99.5 percent pure. It is further refined to attain purity as high as 99.999 percent, but the chemical processes for this are proprietary (8).

5.2 ARSENIC PRODUCTION AND PURIFICATION

Arsenic is produced in a trioxide form as a byproduct of copper and lead smelting and is contained in the flue dusts from these operations. The flue dusts, containing 10 to 30 percent arsenic, are roasted at 400°C (752°F), at which temperature the arsenic vaporizes. This is followed by condensation of the vapor to produce arsenic trioxide of 90 to 95 percent purity. This crude arsenic trioxide is resublimed in a reverberatory furnace at 550°C (1022°F) and then passed through a series of condensing chambers of gradually decreasing temperature. The purity of the arsenic trioxide obtained may range from 94.9 to greater than 99 percent (8,68). Arsenic metal may also be produced from the trioxide by reduction with charcoal, followed by condensation of the metal vapor (8,68). Figure 5-2 shows a simplified flow diagram for arsenic production.

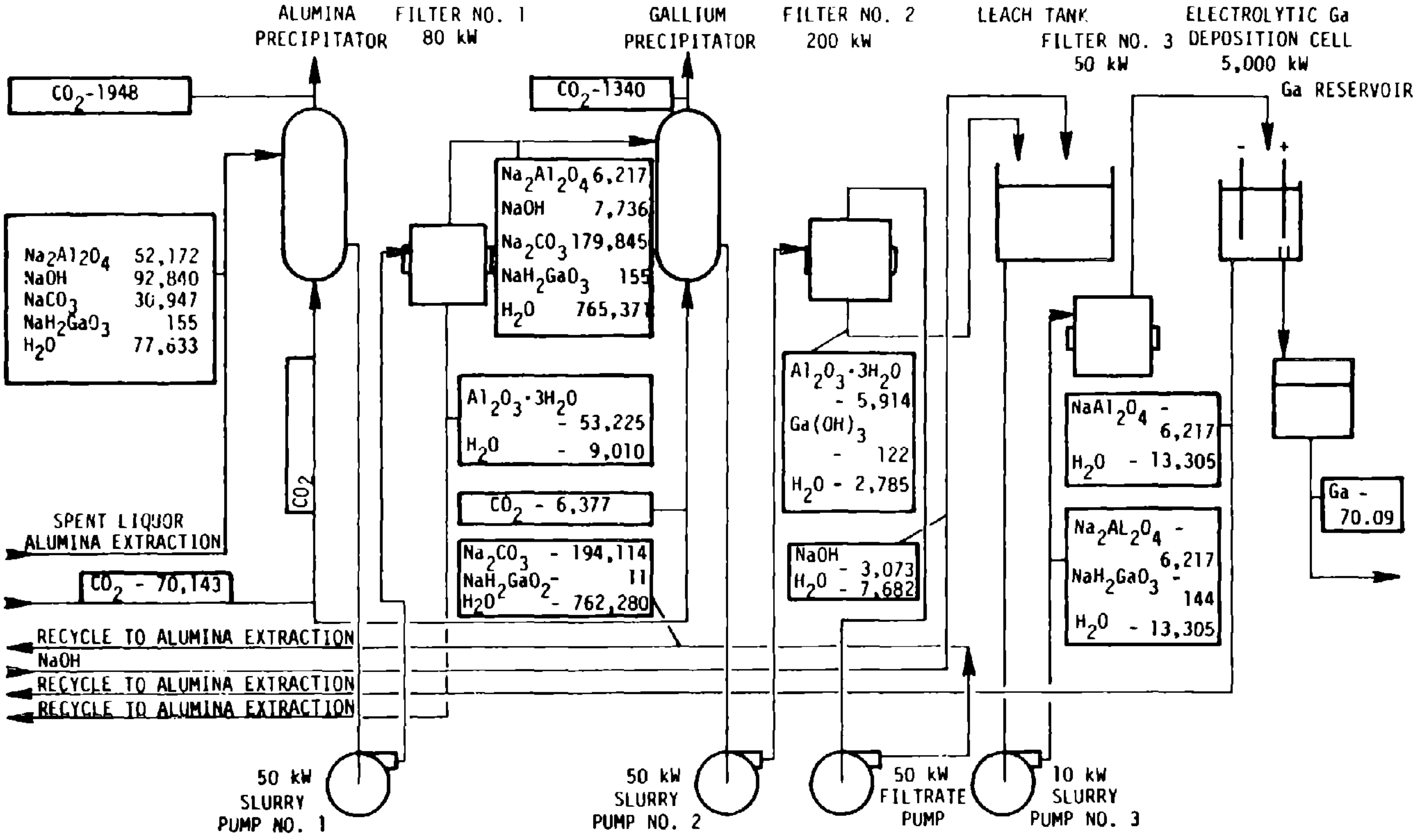


Figure 5-1. Process flow diagram for gallium production (Ref. 8)

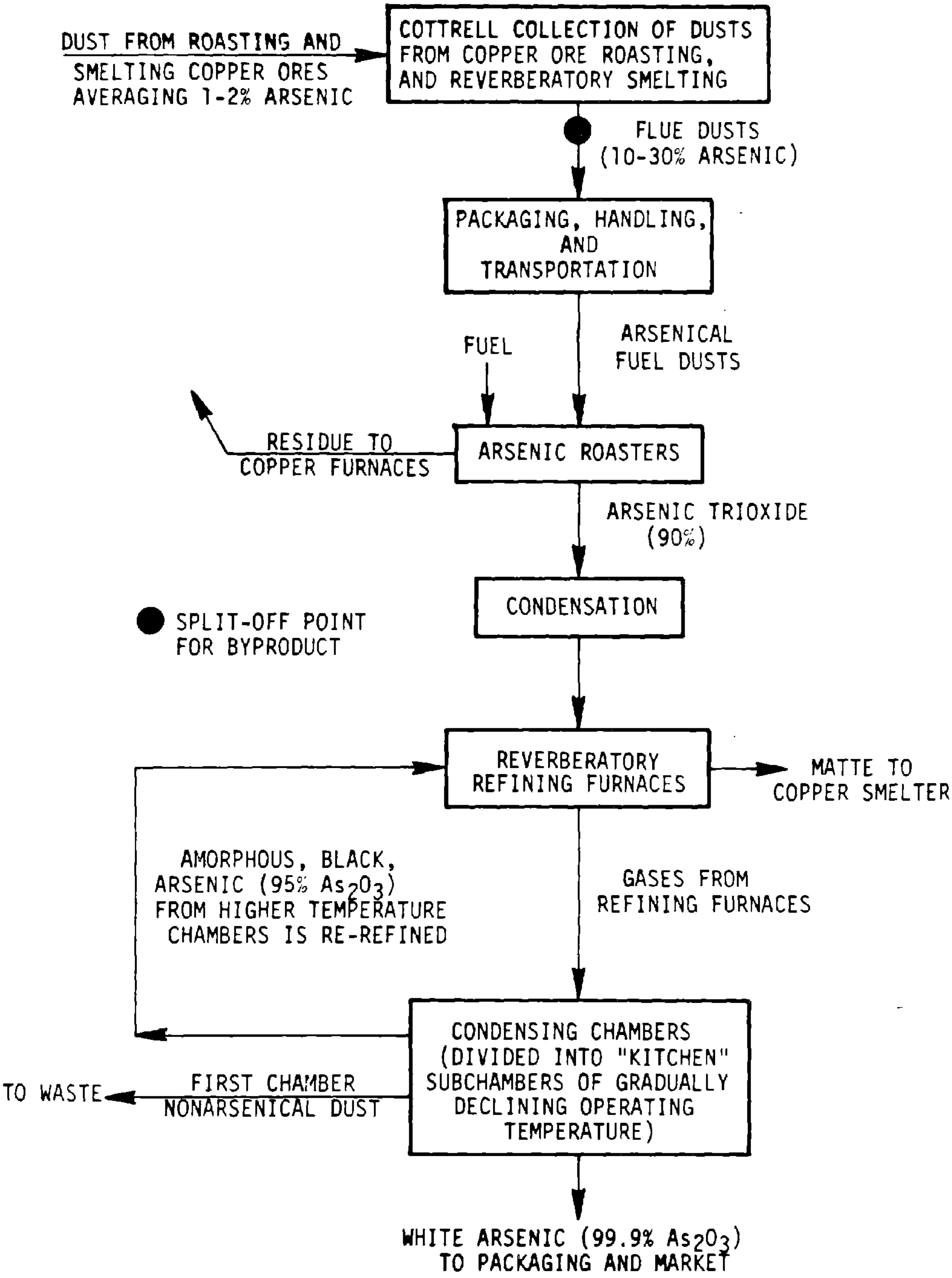


Figure 5-2. Arsenic production from flue dusts (Ref. 8)

5.3 GALLIUM ARSENIDE CELL FABRICATION

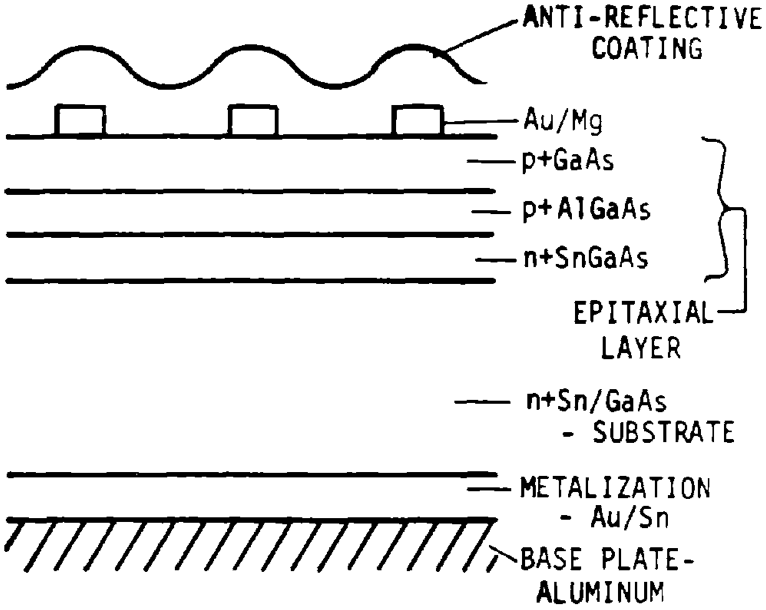
Two basic types of GaAs cells are being developed. The major effort has been in the development of the single-crystal GaAs cell on which GaAs and AlGaAs layers are grown by liquid-phase or vapor-phase epitaxy (LPE and VPE). The single-crystal GaAs cell will be used in concentrator systems. Another type of GaAs cell being investigated is the thin-film polycrystalline GaAs cell. Because of the high absorption coefficient of GaAs, the thin-film cell is being investigated for use in flat panel solar arrays. Intensive research and development to improve the GaAs cell has generated a number of cell designs.

5.3.1 Single Crystal GaAs Cell

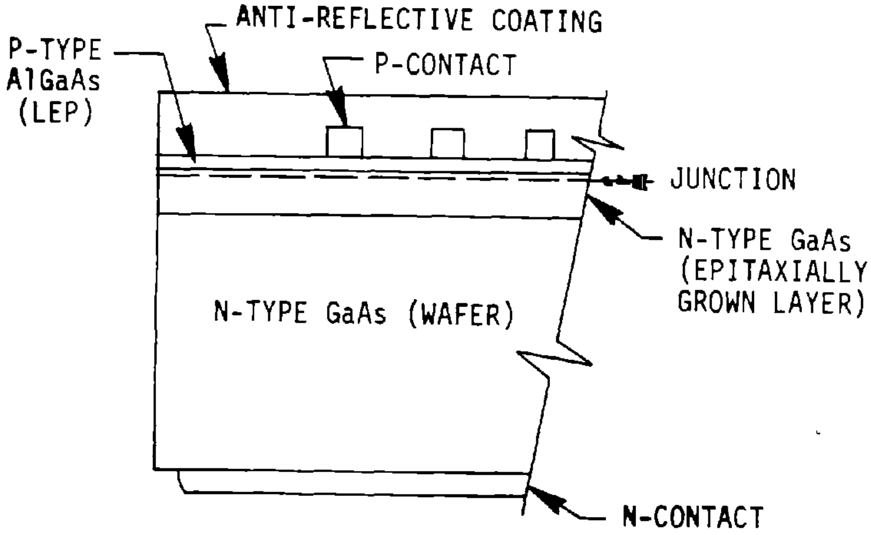
Four designs for single-crystal GaAs cells are shown in Figure 5-3. With the exception of Figure 5-3d, these cells are all of the heterostructure GaAs/AlGaAs type, with various modifications. The cell in Figure 5-3d, is a homojunction cell constructed without the AlGaAs layers.

The first step in the fabrication of single-crystal GaAs cells is the synthesis of polycrystalline GaAs. Gallium in chunk form is loaded in a quartz boat and placed at one end of a long glass tube. Crushed metallic arsenic is loaded into the other end of the tube, and both ends are sealed in vacuum. The tube on a roller assembly enters a two-zone tube furnace. The arsenic end is maintained at 610° to 620°C (1130° to 1148°F), while the gallium end is kept at 1250°C (2282°F) [melting point of GaAs is 1238°C (2260°F)]. The arsenic vaporizes and reacts stoichiometrically with molten gallium to form GaAs. At GaAs melt temperatures, gallium may react with the quartz (SiO_2) boat to form gallium oxide (Ga_2O) (8). The large temperature gradient maintained over the glass tube prevents transport of the Ga_2O and thus contamination of the GaAs. Free silicon is also produced; it is prevented from contaminating the GaAs by maintaining a high vapor pressure of Ga_2O (8). Residual arsenic in the bottle is held to a minimum by adding less than the stoichiometric amount of arsenic (8).

The resultant polycrystalline GaAs is next placed in Czochralski single-crystal pullers to provide single-crystal GaAs for photovoltaics. The chunk GaAs is loaded into a quartz ampule with an outer graphite receptor. It is then melted at temperatures close to 1238°C (2260°F), and the crystal is pulled in a pressurized atmosphere of close to 90 MPa (100 atm) (8). A liquid B_2O_3 blanket is maintained over the GaAs to help control vapor pressure. While the single-crystal GaAs is growing, it is doped to make it n-type GaAs. Dopants include tin (72), germanium (8,72), and tellurium (7,72). Ingots produced by this method are up to 6 cm (2-1/2 in.) in diameter.



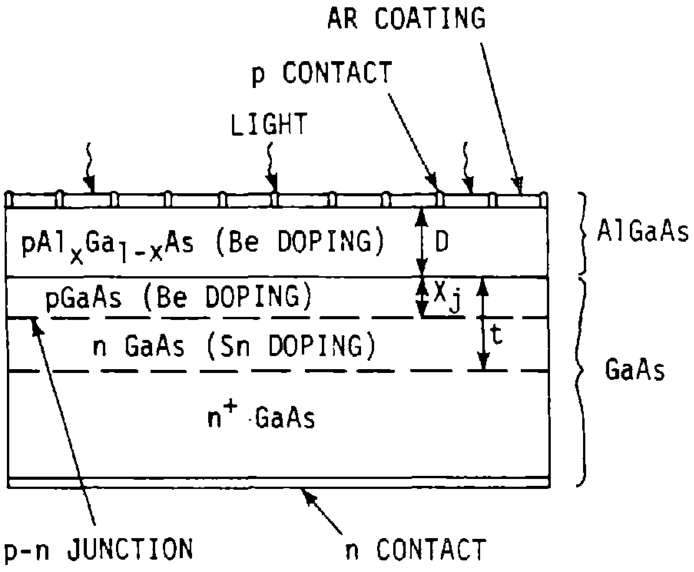
a. (Ref. 69)



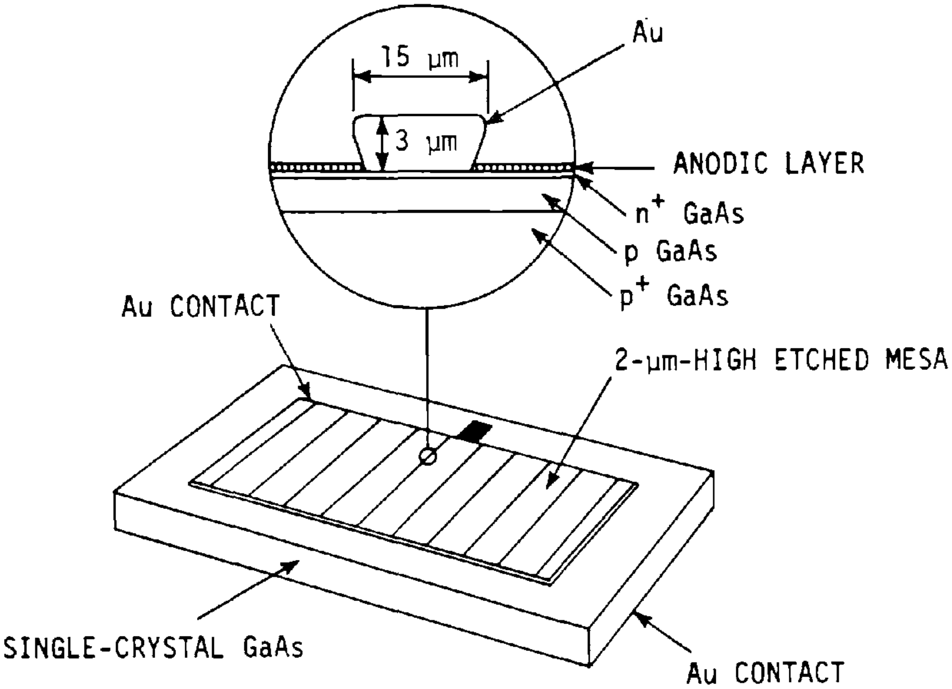
(continued)

b. (Ref. 8)

Figure 5-3. Single crystal gallium arsenide cells.



c. (Ref. 70)



(d) Single-Crystal GaAs shallow homojunction cell (Ref. 71)

Figure 5-3 (continued)

An ingot puller capable of producing ingots about 7.6 cm (3 in.) in diameter is to be installed at Plant L. This puller will operate at 6.9×10^5 to 1.03 MPa (100 to 150 psi) and 1225°C (2237°F) with a boron oxide cover layer over the GaAs melt to prevent arsenic loss. An inert blanketing gas will also be used in the chamber. After the single-crystal GaAs is grown, it is sliced into wafers, usually with reciprocating multiple-band saws (8,72) or water-cooled diamond saws (8). The wafers are then cleaned with a solution consisting of hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_2), and water (8,73). Prior to this cleaning Plant L cleans the wafers in solvents in the following sequence: trichloroethylene, acetone, methyl alcohol, and isopropyl alcohol to dry. Each solvent is used to remove different organic residues. These operations are performed by dipping a group of wafers in a holder into beakers of solvent under a laboratory hood. After the H_2SO_4-H_2O_2 etch, the wafers are rinsed with water and dried with isopropyl alcohol. The resulting n-GaAs wafers are of high quality and purity but have poor diffusion lengths, which reduce the response to long-wavelength light (8). These substrate defects are overcome by depositing an n-doped GaAs by layer liquid phase epitaxial growth (LPE). In liquid phase epitaxial growth preweighed metal is added to graphite chambers positioned in an enclosed quartz tube. In one process, the quartz tubes are guided part way into a cylindrical Marshall furnace, far enough to heat a multi-compartment boat. The metal melt is allowed to equilibrate and then the melt is positioned over the substrate and the furnace temperature is lowered to form the GaAs layers. After growth, the wafers are ready for cell processing. The LPE melts contain approximately 99 percent Ga and are recycled by the Ga supplier to recover the Ga.

Plant N has designed a semiautomatic technique for sequentially positioning the wafer in a holder under the graphite chambers and placing the cylindrical furnace over the glass tube to melt the metal. After a series of melts the different layers are built up. During a melt the temperature, which is at 800° to 900°C (1472° to 1652°F), is reduced for addition of a new layer. The layer forms by crystallographic condensation. A hydrogen purge is maintained in the tube, which is under vacuum. The hydrogen is exhausted through an oil bubbler into a vent duct.

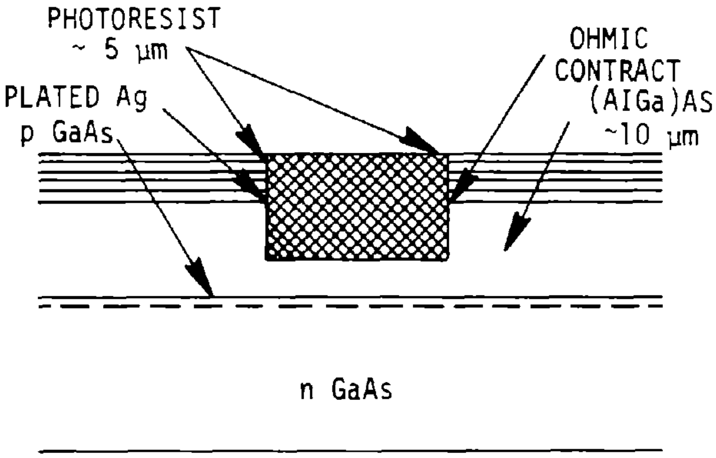
The LPE assembly is equipped with temperature control overshoot. Gallium and arsenic are contained in the graphite, and any arsenic vapor escaping into the hydrogen is condensed on the glass walls, a very small amount being collected in the oil bubbler.

In yet another LPE process, the GaAs is placed in a graphite boat that has been heated in vacuum at 1400°C (2552°F) for several hours (8). The n-GaAs is soaked for 2 hours in a purified hydrogen atmosphere at 847°C (1557°F). The melted n-GaAs is then brought into contact with the heated GaAs wafer. The temperature of the system is reduced at a controlled rate, and the n-GaAs crystallizes from the melt onto the substrate (8). This first LPE layer of GaAs is n-doped. Dopants are tin (7,70,72), tellurium (7), or silicon (7,8,74).

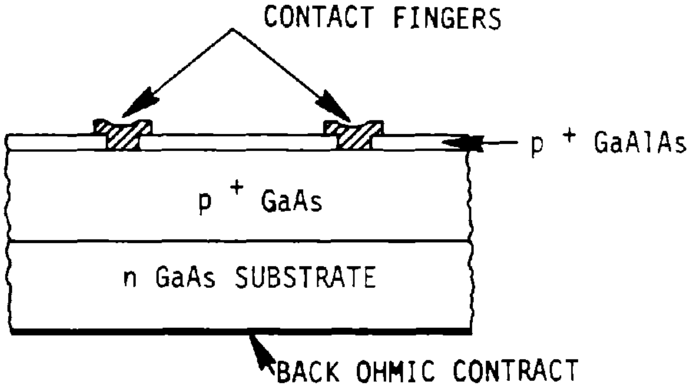
The next layer is also deposited by one of the LPE processes described above. This layer is p-doped AlGaAs. The dopant may be beryllium (70), magnesium (72), germanium (7), or zinc (7). The dopant used by Plant N is proprietary. The LPE growth of the AlGaAs onto the n-GaAs substrate results in the formation of a p-n junction. The p-n junction is obtained by allowing the p-dopant to diffuse into the n-GaAs, resulting in a p-GaAs section (see Figure 5-3a).

The depth to which the p-dopant diffuses into the n-GaAs layer is determined by the growth time of the p-AlGaAs layer (70). The depth of this p-n junction should be approximately 1 µm below the AlGaAs/GaAs heterojunction (70,72). This resultant AlGaAs/GaAs heterojunction confines electrons generated in the p-GaAs section, giving low surface recombination velocity, which increases efficiency over that of a straight GaAs cell (8). The AlGaAs window layer reduces surface and series resistance of the cell, resulting in higher current collection efficiency at short wavelengths (8,64). Because of the high aluminum activity in the AlGaAs, the surface oxidizes upon exposure to air (64,70). This oxide layer causes a high and unstable specific contact resistance value (64), making direct application of metal contacts to the AlGaAs surface unsatisfactory. To alleviate this problem one manufacture grows a 1-µm-thick lattice matching layer of p-GaAs immediately after the AlGaAs layer has been deposited (70). Any material with which high p-type doping can be obtained along with high conductivity and lattice match is suitable (70). This cell is shown in Figure 5-4a.

An alternative to LPE junction formation is vapor-phase epitaxial growth (VPE). In this alternative junction formation technique, the materials needed in a layer are metered with mass flow controllers into a stainless steel manifolded mixing chamber as organometallic gases. Gases are stored in cylinders. Gases used include trimethylgallium [$(CH_3)_3Ga$], trimethylaluminum [$(CH_3)_3Al$], diethylzinc [$(C_2H_5)_2Zn$], arsine (AsH_3), HCl, H_2S, and hydrogen carrier gas. Wafers are loaded onto a coated graphite surface in the reaction chamber. The chamber is cold walled, with growth only at the hot zone. The chamber is wrapped with RF coils to control temperature. The gas mixture is metered into the chamber at atmospheric pressure; the organometallics disproportionate into metals, releasing the hydrocarbons. The metals and dopants deposit out to form an epitaxial layer on the wafers, and the gas is exhausted to a sequence of scrubbers. The reaction chamber develops a thick buildup, which is cleaned with aqua regia.



a. (Ref. 20)



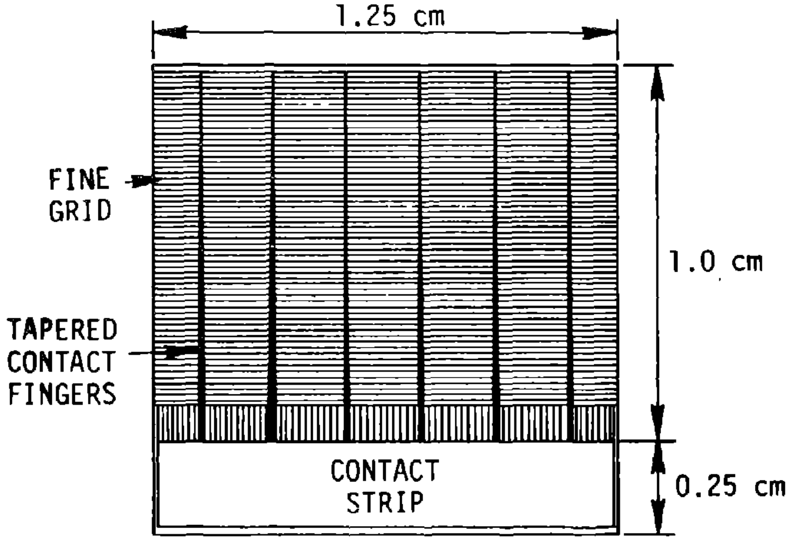
b. (Ref. 64)

Figure 5-4. Contact configurations.

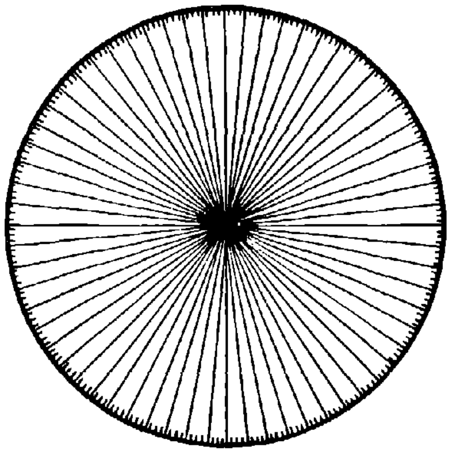
After the final layer (either AlGaAs, or GaAs) has been deposited, the front contact is applied. The front contact grid pattern is first developed by use of photolithographic techniques (64,70,72). Composition of the photoresists is not reported. In one case an SiO_2 protective coating is applied by chemical vapor deposition prior to the application of photoresist (72). After the contact pattern is developed, it is etched. If GaAs is the top layer, it is entirely etched away except where the contact will be. The cell in Figure 5-4b has the pattern etched through the SiO_2 layer to the p-GaAs layer (72). The cell in Figure 5-4a has the pattern etched a few micrometers into the AlGaAs layer (70). One etchant reported is a hydrogen bromide-bromine solution. After the grid pattern has been etched, the front ohmic contact, usually consisting of germanium (75), silver-zinc (7,64), gold-zinc (7,70), palladium (7), palladium-silver (74), or gold-magnesium (72), is deposited by vacuum evaporation. This is followed by electroplating a layer of silver (64,70) or gold (72) on top of the ohmic contact to increase the conductivity of the grid. Some grid designs are presented in Figure 5-5.

Following contact deposition the excess metal and photoresist are removed (72). In one case the contact is sintered at 450°C for 10 seconds in a hydrogen atmosphere, followed by the removal of the remaining SiO_2 and p-GaAs layers with a solution of ammonium hydroxide (NH_4OH) and hydrogen peroxide (H_2O_2) in water (72). An antireflective coating is then deposited on the cell by spray deposition, chemical vapor deposition, or E-beam evaporation to reduce optical losses. This coating may be Ta_2O_5/SiO_2 (64), Ta_2O_5, (70) Si_3N_4 (72), or TiO_2 (7). The back contacts, which may consist of gold-germanium-nickel (7,70), gold-tin (72), tin (7), silver-germanium, platinum, chromium, or thallium, are usually vapor-deposited. The cell may then be bonded to a heat sink [aluminum (64) or gold-plated molybdenum (72)] with a highly conductive silver epoxy (64), or by soldering (72).

Another solar cell being developed uses single-crystal GaAs as the substrate, but does not use AlGaAs to form a heterojunction; this cell is referred to as a shallow homojunction solar cell (71). A schematic diagram is shown in Figure 5-3d. This cell consists of a single-crystal wafer of zinc-doped, p+-GaAs, upon which are grown by chemical vapor deposition (CVD) in an $AsCl_3$-Ga-H_2 atmosphere, p-GaAs (zinc-doped) and n+-GaAs (sulfur-doped) layers, in that order (71). An antireflective coating is then prepared by anodization of the n+-GaAs layer with an electrolyte solution consisting of H_2O, NH_4OH, and propylene glycol. The remaining n+-GaAs layer is extremely thin so that most of the carriers are generated in the underlying p-GaAs layer, thereby reducing surface recombination losses (71). Front contact patterns are also produced by photolithographic techniques. The contacts, both front and back, are of electroplated gold. After



a. Front grid pattern for a rectangular concentrator cell (Ref. 64)

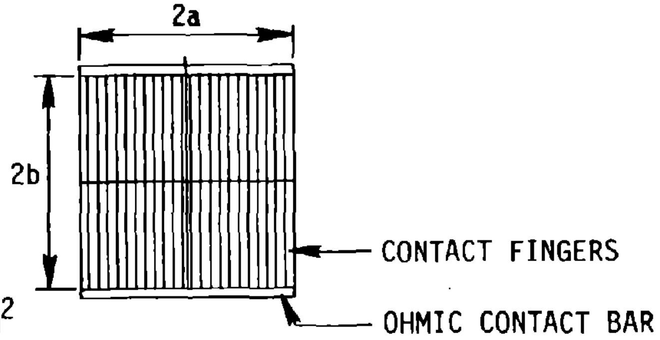


The front grid pattern for the 1 cm diameter concentrator cell. It consists of 256 tapered radial grid lines leading to the outer contact ring.

b. (Ref. 64)

DESIGN PARAMETERS

SIDE LENGTH	$2a = 1$ cm
FINGER SPACING	$b = 250$ µm
FINGER WIDTH	$w = 20$ µm
FINGER HEIGHT	$h = 10$ µm
REQUIRED CONTACT RESISTANCE	$R_{cl} < 10^{-4}\ \Omega\text{cm}^2$



c. (Ref. 70)

Figure 5-5. Grid patterns for AlGaAs/GaAs concentrator cells.

contact application the wafer is annealed in N_2 for 1 second at 300°C (572°F) to produce ohmic contact between the gold front contacts, and the n+-GaAs layer (71). Conversion efficiencies of up to 20 percent were measured for these cells (71).

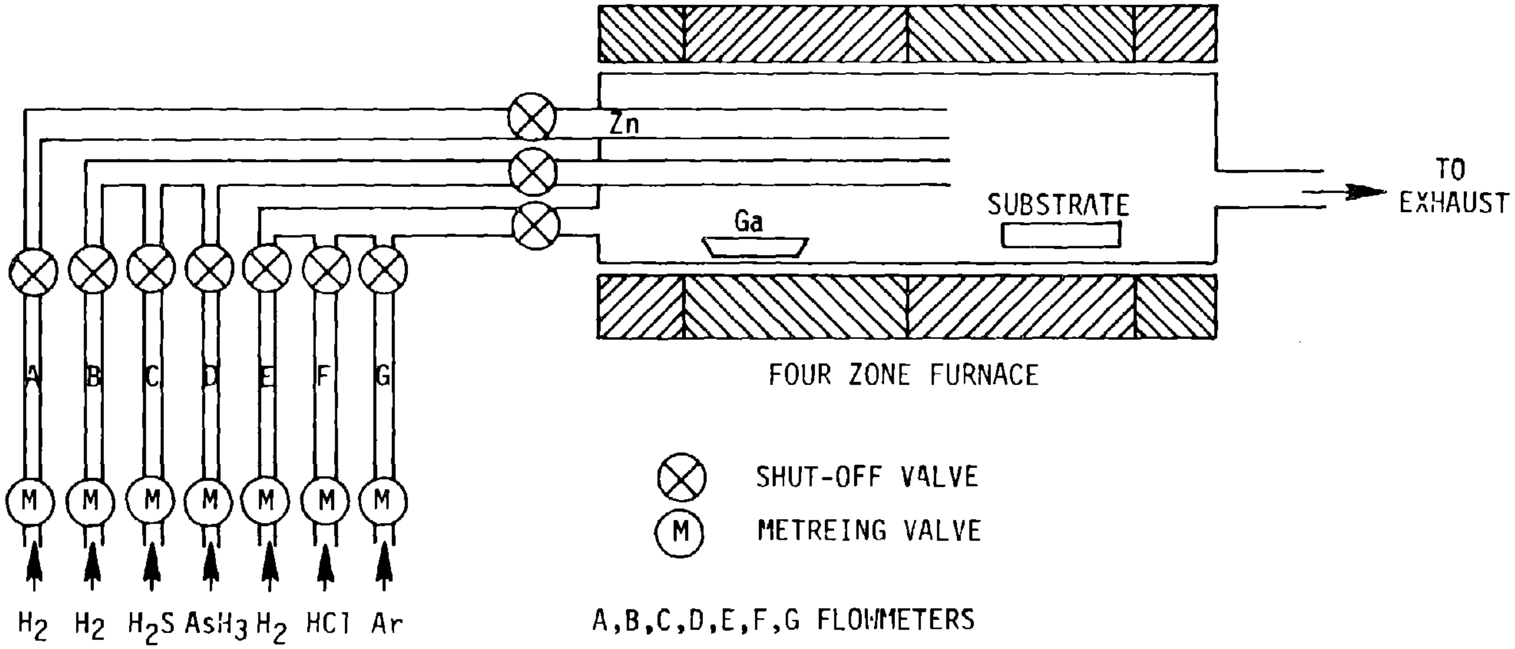
5.3.2 Thin-Film Polycrystalline GaAs Solar Cells

Recent advances in deposition techniques and development of suitable substrates for deposition have generated increased interest in thin-film GaAs solar cells. Because of the high absorption coefficient of GaAs, essentially all of the solar radiation is absorbed within the first few micrometers of the surface, and thus this material is an excellent candidate for use in thin-film cells.

The first thin-film GaAs cells were constructed in 1967 by use of a chemical transport technique to deposit the GaAs films on molybdenum and aluminum substrates (7,76). Various other technologies for deposition of GaAs thin films have been developed. One is a vapor-phase epitaxial (VPE) (i.e., chemical vapor deposition) process whereby GaAs films are deposited by reaction of gallium with hydrogen chloride and arsine in a hydrogen atmosphere (76,77). Another is a metalorganic chemical vapor deposition (MO-CVD) process whereby metalalkyl trimethylgallium (TMGa), and the hydride arsine, AsH_3, are mixed in the gas phase in a reactor and passed over a substrate heated to 700° to 750°C (1292° to 1382°F) (78,79). By substitution of TM-Al for part of the TM-Ga, an AlGaAs layer may be formed. Dopants used include diethyl zinc (DE-Zn), which is a p-type, and selenium hydride (H_2Se), which is an n-type (71,80). A schematic diagram of the VPE deposition process is shown in Figure 5-6.

In the VPE deposition of GaAs a graphite substrate was used, onto which an interlayer of tungsten had been deposited. The tungsten was deposited by the thermal reduction of tungsten hexafluoride in a hydrogen atmosphere (76,81). A Schottky barrier cell was constructed by first depositing a layer of n+-GaAs, followed by a layer of n-GaAs. Gallium arsenide films that are VPE-deposited are inherently n-type, and at higher temperatures [e.g., about 775°C (1427°F)], carrier concentrations can be increased by decreasing the AsH_3/HCl molar ratio (76). Immediately after deposition of the GaAs layers, a thin continuous oxide film is formed. Schottky barrier cells have a lower open-circuit voltage (V_{oc}) than p-n junctions, and the addition of a thin oxide layer increases the voltage output (76). Best results in forming the oxide layer were obtained by in-situ oxidation in an argon-oxygen atmosphere for 0.5 hour at 200°C (392°F), followed by transfer to a glass tube through which oxygen saturated with water vapor flowed at room temperature (76). The cells were kept in the tube for 5 to 30 hours. Following the oxidation process a thin

SCHEMATIC DIAGRAM:



REACTIONS:

$2Ga(\ell) + 2HCl(g) \text{---} 2GaCl(g) + H_2(g)$ (GALLIUM ZONE, 370-910 °C)

$GaCl(g) + AsH_3(g) \text{---} GaAs(s) + HCl(g) + H_2(g)$ (SUBSTRATE ZONE, 720-780 °C)

Figure 5-6. Vapor phase epitaxial deposition apparatus for GaAs thin-film solar cells (Ref. 81) barrier layer of gold or silver was evaporated onto the surface, with subsequent evaporation of a silver grid contact through a metal mask (76). The cell was completed with addition of an antireflective TiO_2 film, deposited by hydrolysis of tetraisopropyl titanate in an argon atmosphere. Cells with an area of 9 cm^2 (3.5 in^2) and AM1 efficiencies of about 6.5 percent have been reproducibly prepared in this manner (76).

The MO-CVD of GaAs has been studied on a variety of substrates, including glass, glass-ceramics, polycrystalline silicas, and composite substrates (80). The composite substrates, which have received the most attention, include germanium films on glass or iron/nickel alloys such as Kovar,^{R*} molybdenum sheets, or molybdenum films on glass or Kovar, graphite, and tungsten/graphite (71,80,82). Among these composite substrates, those that have shown the best results for use in GaAs thin-film cells are molybdenum and molybdenum-coated glass (71).

Two methods for increasing the grain size of the GaAs have been proposed (71). One is by the chemical vapor deposition of germanium polycrystalline films using GaH_4. The other is addition of HCl during the MO-CVD growth process.

Jet Propulsion Laboratories are developing a thin-film GaAs solar cell, shown in Figure 5-7 (82). In this cell an amorphous germanium film is first deposited by vacuum evaporation on the heated substrate, which is an iron/nickel alloy such as Kovar, or on sheet tungsten or tungsten/carbon composites. The germanium is then recrystallized by moving a focused laser beam spot from edge to edge of the wafer while the wafer is being pulled perpendicular to the movement of the laser. The germanium films are doped with antimony. In fabrication of these cells, MO-CVD of GaAs is preferred over VPE with HCl as the transport chemical.

After the GaAs film is deposited, it is partially oxidized by conventional antireflective metal oxide semiconductor techniques. On the cells fabricated, a silver coating was deposited as the barrier metal, although nickel and copper are other candidates. The metal used for contacts is not specified but would be a solderable metal, such as a silver alloy. For this cell, a 4.8 percent efficiency was measured with an AM1 simulator. Speculation is that with an antireflective coating of tantalum oxide (Ta_2O_5), niobium oxide (Nb_2O_5), or antimony oxide (Sb_2O_3), an AM1 efficiency of approximately 8 percent could be obtained.

Another method of GaAs deposition/crystallization is in experimental stages (83). This involves deposition of amorphous GaAs on a suitable substrate (fused silica was used initially), and then crystallization of the GaAs with a laser. Initial analysis

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*Trademark of Westinghouse Corp.

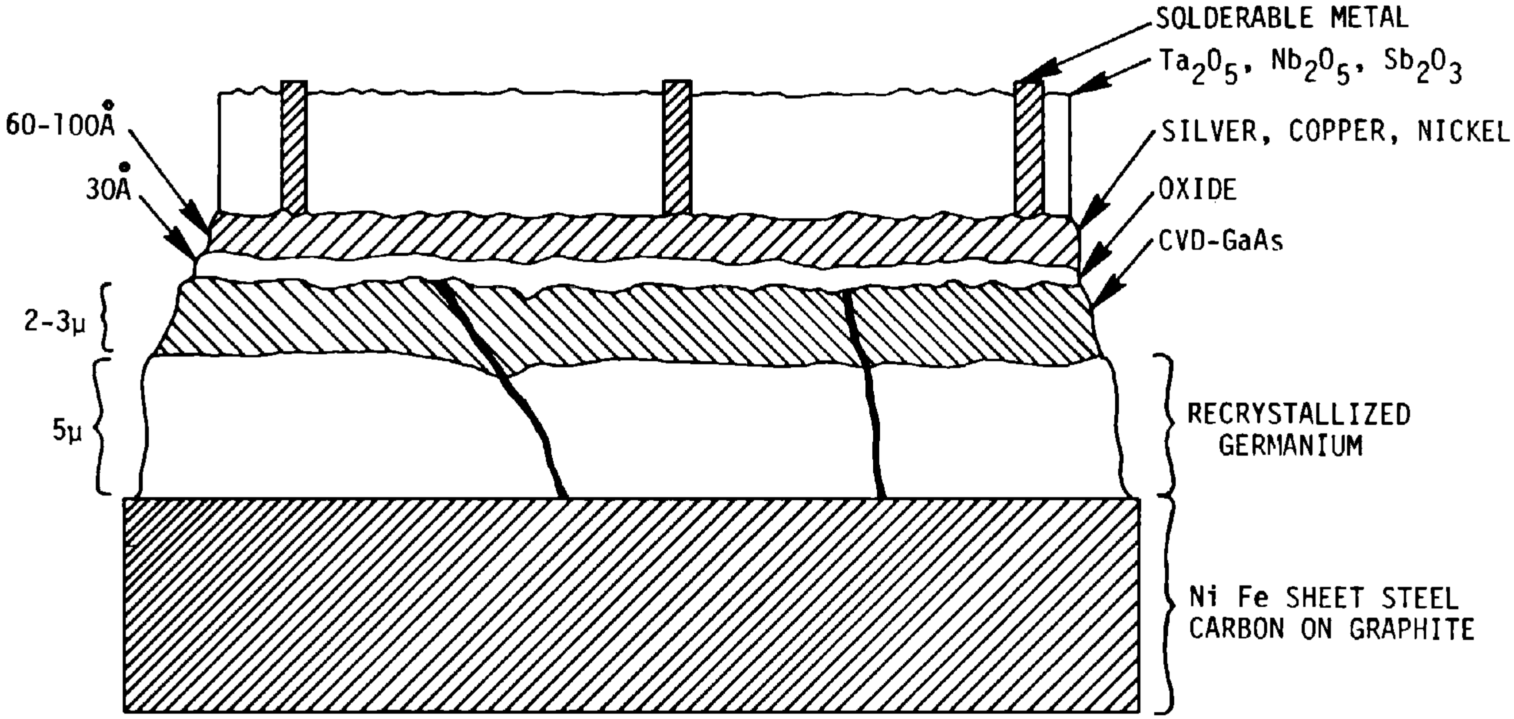


Figure 5-7. JPL GaAs solar cell (Ref. 82)

of treated films did show sharp X-ray peaks characteristic of crystalline GaAs with a preferred orientation. Few details were found on the progress of this method.

5.4 INDUSTRIAL HYGIENE CONCERNS

Gallium arsenide cells are presently produced on a small scale, primarily for research purposes by highly trained and experienced technicians and scientists. The technology is sophisticated, and because of the high cost and toxicity of many materials handled, the techniques for materials containment and recovery are elaborate. Health hazards are also minimized by the relatively small raw materials requirements of the process. In a production facility, however, many personnel would not be highly trained, and the quantities of materials would be much greater.

The potential for arsenic exposure is the most prominent hazard in production of GaAs solar cells. Potential routes of exposure are cleanup of As_2O_3 outside single-crystal puller melts, failure or damage to system components, and handling of waste materials from the following:

- Arsenic cleaned from outside Czochralski melts.
- LPE oil bubbler solution.
- VPE scrubber solution.
- VPE reactor wall cleanup.

Potential for exposure to metals also occurs when the evaporation chambers are cleaned. As in production of single-crystal silicon solar cells, production of single-crystal and thin-film GaAs cells involves the use of organic solvents, acids, bases, and oxidants for etching and cleaning purposes. In the two facilities observed, these operations were performed under exhaust hoods.

A variety of dopants are used in single-crystal and thin-film GaAs cells. These are used in extremely small amounts, and consequently the health hazard is minimal. Beryllium, however, is highly toxic and is a suspect carcinogen as is selenium hydride Because of the high toxicity of these substances, alternative dopants should be seriously considered. Though not quite as dangerous as beryllium and selenium hydride, antimony hydride or stibene is also very toxic; if possible, an alternative dopant should be used.

Little is known of the toxicity of some of the organic-metallic compounds used in fabrication of thin-film GaAs. Though they are used in small quantities, the toxicity of these chemicals, both acute and chronic, are in need of further study. Most organic metabolic compounds burn spontaneously in air, mandating the need for control methods to prevent leaks or discharge into the workplace. Also in production of thin-film

GaAs, arsine (AsH_3), an extremely toxic gas, is used. Although small amounts are used in the thin-film deposition, the TLV is only 0.2 mg/m^3 (0.05 ppm). Special precautions should be taken in areas where arsine is used to prevent possible leaks.

Plant N has developed several engineering and safety precautions to minimize the hazards involved in GaAs cell production. To prevent arsenic exposure during loading, the arsenic is transported in glass ampules in the specific quantity needed. In the polycrystalline GaAs process, a temperature controller is used on the quartz tube apparatus and is automatically shut off in the event of a temperature overshoot. After the glass tube is rolled into the furnace, the hood is closed for the remainder of the cycle.

Plant N takes precautions in the single-crystal GaAs pulling area to isolate the pullers from the rest of the building in case of accidental release. Crystal growing is conducted in a well-ventilated room having a steel door, two concrete block interior walls, and two exterior walls at one end of the research building. Television monitors and electronic instruments track the process, minimizing need to enter the crystal growing room. It is important that this operation be isolated and well-ventilated, because it takes place under pressures greater than 1 atmosphere. The ingot puller to be installed by Plant M will operate at about 3.4 MPa (34 atmospheres). Any leaks in the system could release significant quantities of arsenic in the pulling area.

Cleanup around the crystal pullers includes removing small amounts of arsenic as AS_2O_3 outside the melt. The equipment surfaces are wiped with towels dampened with ammonium hydroxide and hydrogen peroxide.

Liquid and vapor epitaxy are conducted at essentially atmospheric pressure. Process steps are conducted within laboratory hoods. Scrubber systems are used to control effluent emissions, with venting through the laboratory exhaust system. Material flow rates and temperatures are very carefully monitored and controlled.

In the Plant N LPE process, arsenic released from the quartz tube is removed by passage through an oil bubbler and then to an exhaust duct.

At plant N, the exhaust gas from the VPE process passes through the following sequence of chambers:

1. An empty chamber to settle out solids such as GaAs, arsenic, gallium, aluminum, and zinc.
2. An oil chamber to remove additional solid particles.

3. A water solution to collect HCl, H_2S, Ga_2O_3, Al_2O_3, ZnO, and organic metallics.

4. A bromine-water solution, in which AsH_3 undergoes reaction to AsBr and finally to As_2O_3, which precipitates out.

5. An NaOH solution to cause reaction of any bromine carryover to NaBr.

The exhaust gas should be essentially all hydrogen.

The hydrogen supply is kept outside the building. Plant N uses an automatic hydrogen detection system in the area when hydrogen is used. At 0.8 percent ambient concentration, an alarm sounds and the pressure in the supply tanks is dropped to 40 percent of the normal storage pressure. Provisions must be made for any hydrogen exhausted to avoid fire. At 2 percent ambient concentration, the hydrogen supply is shut off. Any sudden change in pressure drop in the hydrogen supply line also will shut off the supply.

At plant N, protective clothing (gloves, glasses, respirators) is reportedly used as necessary during cleaning and handling of the equipment. Cleaning is generally conducted within a laboratory hood. Crystal cutting operations are provided with local exhaust ventilation. Kerf loss is controlled primarily by capture in a wet slurry. Laboratory glass and other materials are sometimes cleaned in a special cleaning area, by trained and experienced personnel.

At plant B, GaAs was produced primarily for use in making light-emitting diodes (LED) for calculators, displays, etc. It was reported, however, that there were some experimental and spacecraft applications of GaAs photovoltaic cells. At this plant gallium arsenide was produced by the reaction of extremely pure gallium and arsenic in resistance heated furnaces by the gradient freeze method. A sampling survey was conducted in this plant for arsenic. A summary of samples and analytical results is given in Table 5-1. The highest personal exposure level was 87.3 $\mu g/m^3$ of arsenic in the GaAs cylinder preparation area. This is still substantially above the TLV of 10 $\mu g/m^3$. Wipe samples were collected by wiping 1 ft^2 of equipment surface. Results were then converted to mg of arsenic per m^2 of surface. Samples ranged from 1.3 to 13.3 mg/m^2. Although there is no standard applicable to these results and no standard procedure for collecting such samples, they are useful in assessing plant cleanliness. It is suggested that work areas with the higher arsenic buildup, such as the arsenic weighing hood top and crucible welding table top, be cleaned more frequently. Poor housekeeping could result inadvertently in contamination of workers' clothing, and possible ingestion, or reentrainment of dust into the air.

TABLE 5-1. SAMPLING SUMMARY SHEET FOR ARSENIC - PLANT B

Sample description	Sample type	Concentration
GaAs wafer slicing	Personal	14.9 μg/m^3
GaAs wafer slicing	Area - near sample taken above	15.0 μg/m^3
GaAs wafer slicing	Personal	11.3 μg/m^3
GaAs wafer slicing	Area - near sample taken above	13.1 μg/m^3
Break-out of GaAs quartz cylinder	Personal	<3.8 μg/m^3
GaAs preparation area	Personal	87.3 μg/m^3
Ingot slicing - cabinet top	Wipe	3.39 mg/m^2
GaAs crucible assembly, As weighing, top of system	Wipe	1.29 mg/m^2
As weighing, hood top	Wipe	13.0 mg/m^2
Crucible welding, table top	Wipe	13.3 mg/m^2

5.5 SUMMARY AND RECOMMENDATIONS

1. Exposure to arsenic is the most obvious hazard. Critical areas of concern are raw materials handling, synthesis of polycrystalline GaAs, single-crystal pulling, cleanup and maintenance of equipment contaminated with arsenic, and handling of waste materials containing arsenic.

2. All processes in which release of arsenic is possible should be isolated and equipped with an automatic shutoff or seal system and/or a backup ventilation system. The two most critical areas are polycrystalline GaAs synthesis, and pulling of GaAs single crystals.

3. Beryllium, selenium hydride, and antimony hydride used as dopants all have very high chronic and acute toxicities. Although it is recognized that the amounts of these substances used are very small, their extreme toxicity still dictates a need to investigate alternative dopants.

4. Very little is known about the toxicity of GaAs dust and fumes, which can be generated in wafer slicing. More information is needed.

5. Toxicity of the organometallic materials used in thin-film GaAs production is virtually unknown and needs further study. Since these materials combust spontaneously on exposure to air, the decomposition products also should be determined and tested for toxic potential.

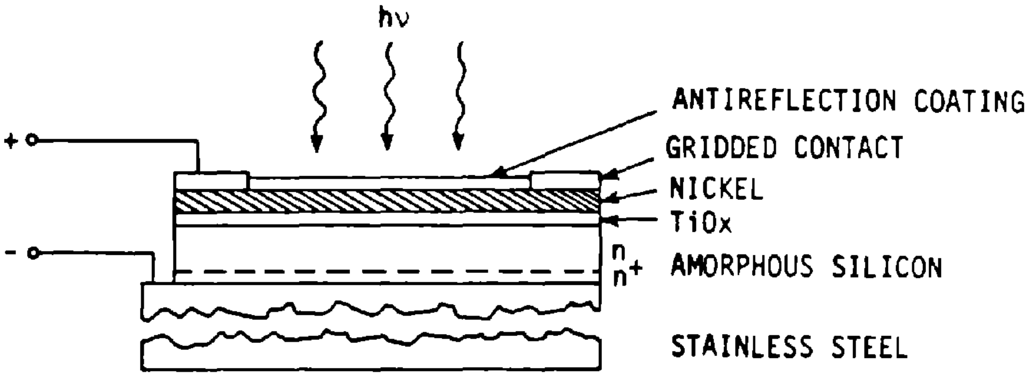
6. Solvent and acid baths should be well ventilated by systems that incorporate fail-safe design with alarms.

6. AMORPHOUS SILICON SOLAR CELLS

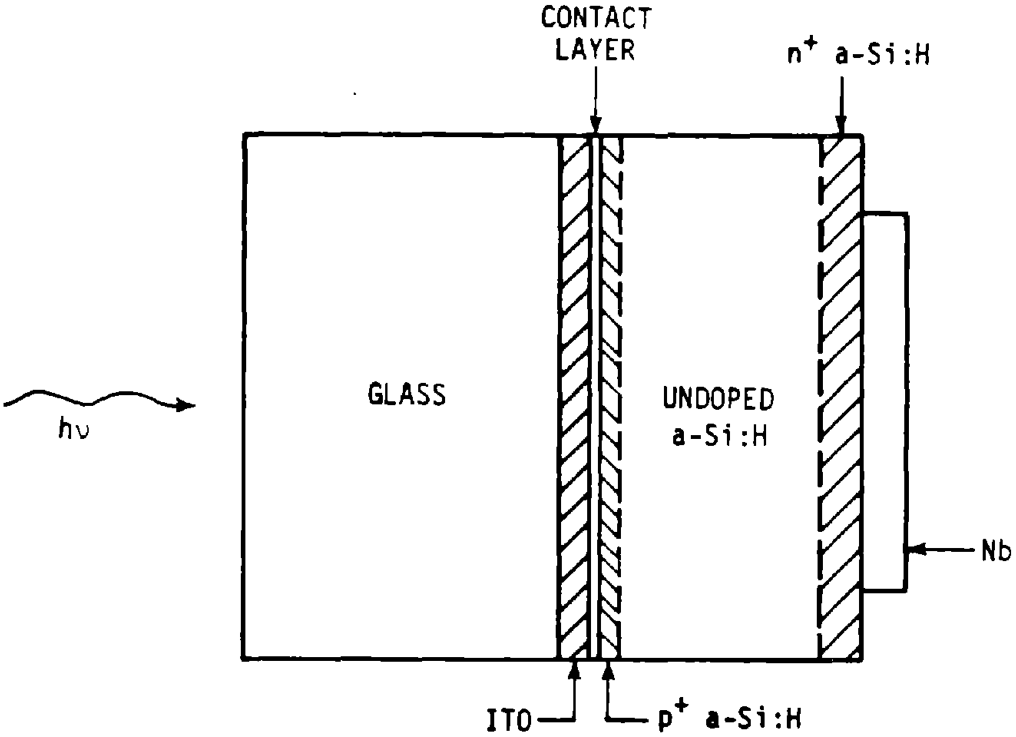
Of the three major processing steps now used in production of solar cell modules (wafer making, cell manufacturing, and module fabrication), the wafer-making step accounts for approximately 70 percent of the cost (84). About 17 to 20 percent of the wafer-making cost is tied up in manufacturing the defect-free silicon slice (84). Two major factors involved in the high cost of the silicon wafer are the production of solar-grade polycrystalline silicon and the pulling of single-crystal silicon ingot (84). These processes are also extremely energy-intensive. One estimate is that 700 kWh of energy is required to manufacture a cell with a peak output of 1 kW (on the assumption that cells are 100 μm thick and that 82 percent of the silicon in the manufacturing process is wasted). One recent development intended to reduce costs of the silicon wafer is the thin-film amorphous (noncrystalline) silicon cell.

A number of efforts toward development of an amorphous silicon solar cell have been reported (85-89). Four basic types of amorphous silicon (a-Si-H) cells have been developed: the M-I-S (metal-insulator-semiconductor) cell; the Schottky barrier cell; the heterojunction cell, and the p-i-n cell. Diagrams of these cells are shown in Figures 6-1 and 6-2.

To date the most promising results have been efficiencies approaching 6 percent in Schottky barrier cells and 4.8 percent in M-I-S cells (87,89). These cells are constructed by first depositing a hydrogenated film (a-Si-H) on heated 300° to 350°C (572° to 662°F) steel or conductive glass substrates (89). The method of deposition has typically been by RF or dc glow discharge decomposition of silane (SiH_4) (85,87,88), although sputter deposition can also be used in some cases (87). The a-Si-H films exhibit defect densities within the energy gap that are several orders of magnitude less than those observed in most amorphous semiconductors (87). The hydrogen, which constitutes approximately 10 to 50 percent of the film, is believed to be partly responsible for the low density of defect states by attaching to "dangling" silicon bonds and thereby minimizing the losses that would occur at these sites (85,87). It is also reported, however, that hydrogen, through its various bonding configurations, can be responsible for localized (defect) states within the energy gap (86). Although in comparison with other amorphous semiconductors,

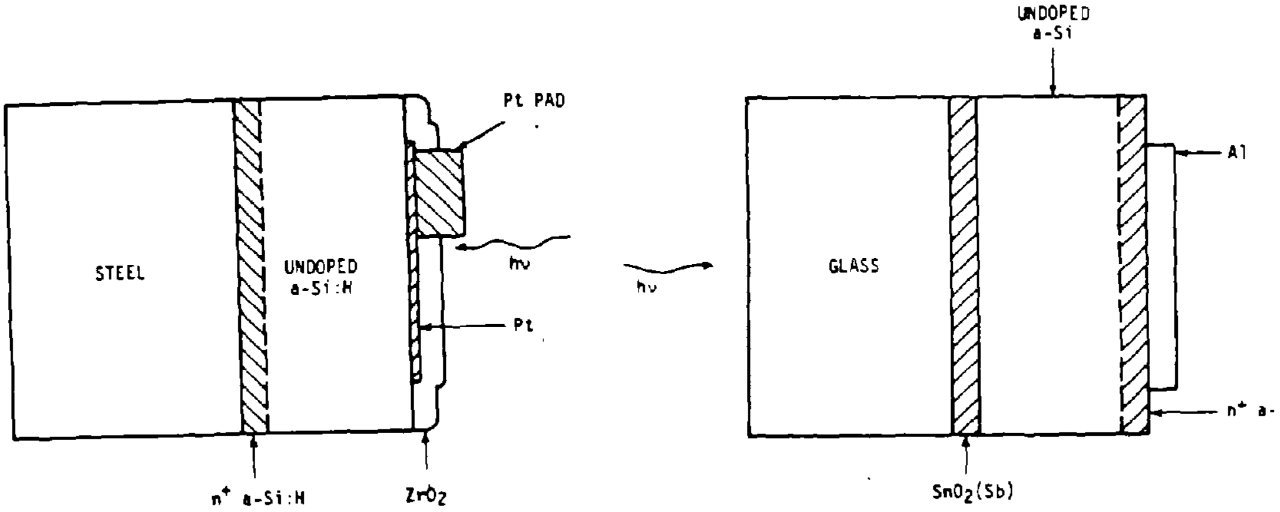


a. Cross-section of MIS solar cell (Ref. 87)



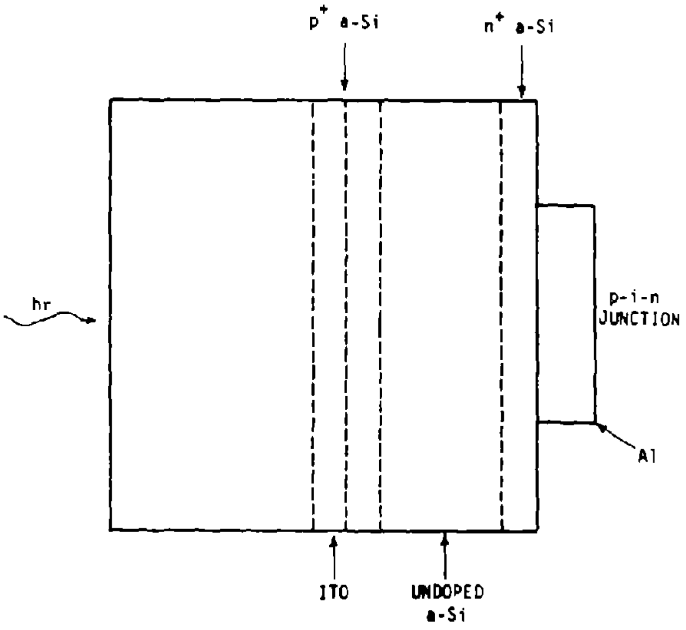
b. Schematic of an MIS solar cell (Ref. 89)

Figure 6-1. MIS amorphous silicon solar cells.



a. Schematic of Schottky barrier cell (Ref. 89)

b. Schematic of hetero-junction (n-n) solar cell (Ref. 85)



c. Schematic of solar cell p-i-n (Ref. 85)

Figure 6-2. Various types of amorphous silicon solar cells.

the glow-discharged a-Si-H films have a low density of gap states, they are still of relatively high density when compared with other semiconductor materials (90). This characteristic leads to inefficient doping and low values for the drift mobility and recombination time of free carriers (86). Ovshinsky and Madan have reported the synthesis of a new alloy having silicon and fluorine as the primary components (86). The new alloy contains only about 0.5 percent hydrogen and may contain oxygen without having deleterious effects on the cell (86). The alloy (a-Si-H-F) is also deposited by RF glow-discharge, but with silicon tetrafluoride (SiF_4) instead of SiH_4. The following are some reported advantages of Si-F-H over Si-H: the room-temperature conductivity and conductive activation energy of Si-F-H are only weakly dependent on the substrate temperature; the room-temperature conductivity of a-Si-F-H is significantly higher (two orders of magnitude) than that of a-Si-H; the estimated activation energy at room temperature for a-Si-F-H is approximately 4 times less and was obtained with dopant levels 1 to 2 orders of magnitude less; and the minimum density of localized states for a-Si-F-H is about 1 order of magnitude less than for a-Si-H. Ovshinsky reportedly has predicted that solar cells made with Si-F-H could be installed in a typical American home to provide power at an amortized cost of $0.05/kWh, which is approximately what consumers now pay (91). No prototype cell has yet been constructed of Si-F-H alloy.

6.1 HETEROJUNCTION a-Si-H SOLAR CELLS

Heterojunction (p-n) a-Si cells have been fabricated by depositing boron-doped (with diborane-B_2H_6) a-Si-H on glass coated with a transparent layer of antimony-doped tin oxide (SnO_2) or indium-tin oxide (ITO) (85). This is followed by deposition of a phosphorous-doped (with phosphine) n-type a-Si-H film. An aluminum electrode is evaporated on the surface of this layer. Another p-n heterojunction cell has been fabricated by first depositing a layer of undoped a-Si on p-type GaAs, followed by deposition of an n-type a-Si-H layer (phosphorous-doped), and finally evaporation of a semitransparent aluminum electrode (85). In both of these heterojunction cells carrier lifetimes have been reduced (and subsequently small short-circuit current densities), apparently because of either clusters of boron or phosphorous dangling bonds on the dopants, or hydrogen bonded to the dopants (85). Under one or more of the above circumstances, traps and recombination centers may be created, in addition to the acceptor and donor levels (85).

An n-n heterojunction cell was constructed by deposition of slightly n-type undoped a-Si-H on a glass substrate coated with SnO_2 (antimony-doped) or ITO followed by deposition of n-doped a-Si-H. The conversion efficiency of these heterojunction cells ranged from only 0.5 to 1.2 percent, with an AM1 light intensity (85).

Another p-n heterojunction cell uses a stainless steel substrate (88). The cell consists of an n-doped a-Si-H layer on the stainless steel followed by an undoped (intrinsic) a-Si-H layer, a p-doped a-Si layer, and a layer of chromium for a contact. No efficiencies were reported.

6.2 SCHOTTKY-BARRIER a-Si-H SOLAR CELLS

Schottky-barrier cells have been constructed by plasma (88) and RF- or dc-induced glow discharge deposition (89) of n-doped a-Si-H on a stainless steel substrate. This is followed by deposition of an undoped a-Si-H layer, and evaporation of a metal contact, either platinum (89) or palladium (88). For large cells a collecting grid is deposited on top of the contact (89). This is followed by an antireflective coating of ZrO_2 or TiO_2 (89).

6.3 M-I-S, a-Si-H SOLAR CELLS

Several types of M-I-S (metal-insulator-semiconductor) solar cells have been fabricated (87-89). In one instance the M-I-S cell is similar to the Schottky-barrier cell except that a thin insulating layer is formed on top of the undoped A-Si-H prior to deposition of the contact layer (89). One M-I-S cell consists of a stainless steel substrate, onto which a layer of n-doped a-Si-H is deposited by RF glow discharge, followed by evaporation of a TiO_x interfacial layer and a semitransparent nickel barrier contact (88). Efficiencies up to 4.8 percent have been recorded for a 0.07 cm^2 cell, and 2.2 percent for a 1-cm^2 cell. Another M-I-S cell consists of a stainless steel substrate coated with successive layers of n-type a-Si-H, undoped a-Si-H, Si_3N_4, and palladium (88).

6.4 p-i-n type a-Si-H SOLAR CELLS

The p-i-n type of a-Si-H cell consists basically of an undoped a-Si layer sandwiched between layers of p-type and n-type a-Si-H. The cells are fabricated by first depositing a thin Pt-SiO_2 cermet (alloy of heat-resistant compound plus metal) film on ITO-coated glass (89). The cermet acts to form a good contact between the ITO and the next layer of p^+-type a-Si. If the p^+-type a-Si-H is deposited directly onto the ITO layer, a thin resistive oxide layer is formed, resulting in poor contact. On the p^+ layer of a-Si-H an undoped a-Si-H layer is deposited followed by an n^+ layer of a-Si-H. A back contact of niobium, titanium, or aluminum is evaporated or sputtered on top of the n^+-type a-Si-H layer to complete the cell (89). Efficiencies up to 2.4 percent are reported (85).

6.5 INDUSTRIAL HYGIENE CONCERNS

Since amorphous silicon is still in the developmental stages, an industrial hygiene assessment is (by necessity) limited. Generally, the main concerns are the same as those in single-crystal silicon cell production. A variety of toxic and/or flammable gases, including SiH_4, SiF_4, B_2H_6, PH_3, and CF_4 are used or will likely be used in fabrication of amorphous silicon cells. It is important that adequate containment and ventilation be provided to prevent the possibility of worker exposure to these gases. Precautions also must be taken to eliminate hazards of fire and explosion. RF and dc glow-discharge decomposition of silane in advanced processes, could present a potential work hazard if adequate shielding is not provided.

A survey of one research facility (Plant J) engaged in fabrication of amorphous silicon cells showed that all equipment was provided with adequate ventilation. Toxic gases were stored in enclosures provided with ventilation by bleed from ductwork running to standard laboratory hoods.

A "research system" being constructed at the facility will be capable of producing amorphous silicon cells in assembly-line fashion. Process pumps as well as gas and chemical tanks are to be located in separate rooms adjacent to the processing area. Both rooms will have separate ventilation systems.

Process pumps are provided with chlorofluorocarbon or fluoropolyether oils, which have extremely long lifetimes, and fiberglass filters on the inlet side. These measures prevent frequent pump maintenance, and thus potential worker exposure to materials that might contaminate the pump.

Generally, the amount of materials used is very small and adequate ventilation should prevent any serious buildup of substances.

6.6 SUMMARY AND RECOMMENDATIONS

1. Among the chemicals now used or having potential use whose toxicology should be better understood are silane, silicon tetrafluoride, and carbon tetrafluoride. Silane is also pyrophoric, and special ventilation is needed to prevent fires and explosions.

2. Dopants such as diborane and phosphine should be carefully controlled and kept in well ventilated enclosures with fail-safe systems. Diborane is also pyrophoric, and special precautions must be taken to prevent fires and explosions.

3. Some metals used for contacts are highly toxic or initial experiments indicate high toxicity. Most antimony compounds are known to be highly toxic. Some niobium salts are highly toxic to animals, but more toxicological information is needed on this metal. More toxicity information is also needed on palladium.

7. INSTALLATIONS

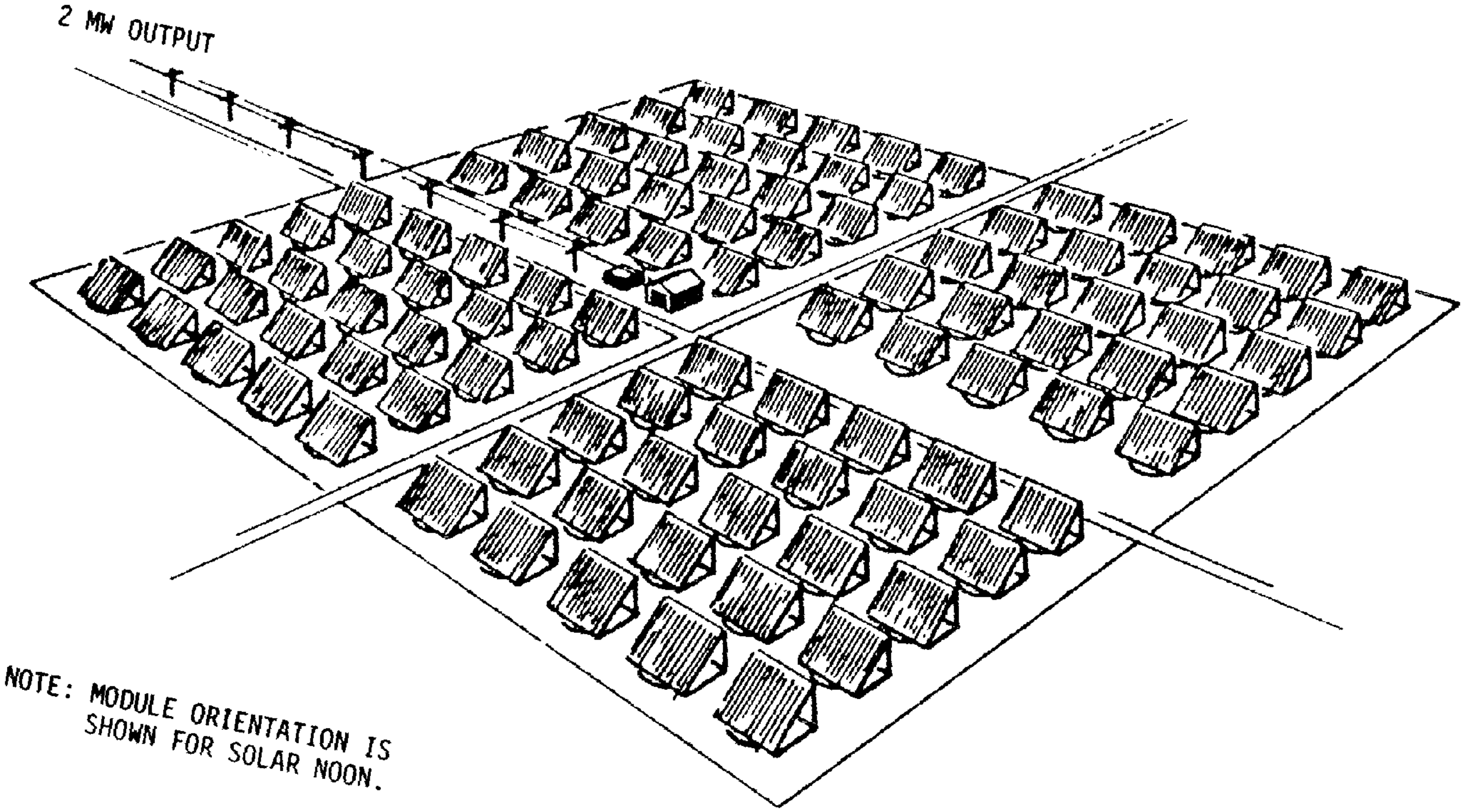
A future goal in photovoltaics is to construct central station power plants that will provide a significant portion of the power requirements in various areas of the United States. The first central power station will most likely utilize flat-plate modules, though concentrating systems may eventually contribute significantly. It has been predicted that flat-plate photovoltaic power plants with arrays costing $100 to $300/kWp will become economically competitive with other power sources in most parts of the United States by the year 2000 (92). For medium- or high-concentration systems to be cost effective by the year 2000, however, profitable uses for the thermal energy generated will have to be found (92). One study concluded that combined usage of a photovoltaic system and a backup energy source (conventional utility) is fundamental to the optimization of terrestrial power systems, and that electrical power could be provided most economically this way (93).

Smaller photovoltaic power systems for industries, schools, airports, and other small-scale applications may also be used increasingly, especially in isolated and rural areas. A number of application experiments are currently testing flat-plate and concentrator systems ranging from 20 to 500 kW.

7.1 CENTRAL POWER STATION COMPONENTS

Unlike conventional central power stations, photovoltaic stations will cover large areas and will be large physically. Flat-plate systems will have large cell areas, whereas high concentrating systems will have large reflecting areas. One hypothetical plant design requires approximately 52 km^2 (32.31 mi^2) (94). This plant consists of 50,000 modules, each 17.1 m (56 ft) long, 8.5 m (28 ft) wide, and 10.4 m (34 ft) high, along with other necessary equipment. The station was envisioned as looking like a city of 50,000 small homes laid out on nearly perfect square grids of 33-m lot lines. A diagram of one group consisting of 100 modules is shown in Figure 7-1.

Though terminology may vary somewhat, the following are the structural classifications in a photovoltaic power system (95):



NOTE: MODULE ORIENTATION IS SHOWN FOR SOLAR NOON.

Figure 7-1. Typical 200 kW solar module group - one of 500 (Ref. 94)

- Cell - the smallest photovoltaic generation unit manufactured individually.

- Module - a group of cells consolidated into a single, handleable unit.

- Panel - one or more modules united structurally into a single field-installation unit.

- Block - the smallest field-assembled generating unit, consisting of structures, foundations, and panels.

- Array - the smallest field-assembled unit operating at the dc (direct current) voltage level of the power conditioning unit.

- Group - a set of arrays with power conditioning and auxiliary systems, achieving power output at the ac (alternating current) voltage level of the power conditioning unit.

- Plant - a collection of groups and auxiliary systems to achieve rated power output at the ac transmission voltage level.

Besides the array structures and land, a station will include three other major components: power plant wiring, power conditioning units, and energy storage. These components will be common to both flat-plate and concentrator systems.

7.1.1 Power Plant Wiring

In one hypothetical 1000-MWp photovoltaic power system, the wiring network consists of four major areas: dc fuses, a 34-kV distribution system, a switchyard, and a 230-kV transmission line (94). The system also includes station power and grounding systems. The 34-kV, 60-Hz ac, three-phase distribution system includes all wiring and components required for connection of each power-conditioning module power output terminal to the 34/230 kV switchyard input terminals on the two 34-kV line dead-end terminus structures (94).

The 230-kV transmission line system includes all wiring, components, and towers required for connection from the 34/230 kV switchyard dead-end structure (94). Terminals and the 230-kV tower structure are located on the plant boundary line and feed into the utility.

Except for the interconnect wiring for the 50,000 modules, the power wing is conventional in amount and design. It is recommended that for interconnect wiring a combination of series-parallel connections should be made at both cellular and modular levels to yield the desired operating current and voltage; in this arrangement the shading or failure of one cell would not reduce modular output to zero, as would be the case if all cells were connected in series (7). The interconnect wiring for the modules will consist of a large amount of relatively small-diameter wire and will be underground. A diagram of the hypothetical switchyard and the general layout of power lines is shown in Figure 7-2.

7.1.2 Power Conditioning Unit

The typical power conditioning module (PCM) consists of a power regulator, a dc-ac inverter, a controller, and a storage battery. In a photovoltaic power plant one PCM will service an array. Figure 7-3 is a block diagram showing how the PCM components tie into the total system.

The function of the regulator is to track, in conjunction with the controller's microcomputer, solar module characteristics for variations in solar input and temperature and to maximize power output for each solar module (94). Since the electrical output from a solar array is of variable dc power, it must be conditioned before it can be used by the consumer. To accomplish this, inverters will convert dc to ac power.

Such inverters have been used for years with uninterrupted power supplies. Their circuit designs are well understood, and modifications for use with photovoltaics are not extensive (96). The modifications would include the addition of a maximum-power tracker and a dc-ac inverter to interface the unit with the variable array voltage. The maximum power tracker will allow the module to operate continually at its maximum power point (7). In one survey of costs of power conditioning equipment (inverter, interface components, and switching), the costs of the power conditioning equipment for a central power station (in 1975 dollars), ranged from $50 to $110/kWp (96).

The controller will be responsible for the mode of operation of the power conditioning module. Seven basic modes of operation are described (94):

1. Group (100 modules) supplies power to battery only.
2. Group supplies power to battery and inverter simultaneously.
3. Group supplies power to inverter only
4. Group and battery both supply power to inverter.
5. Battery alone supplies power to inverter.

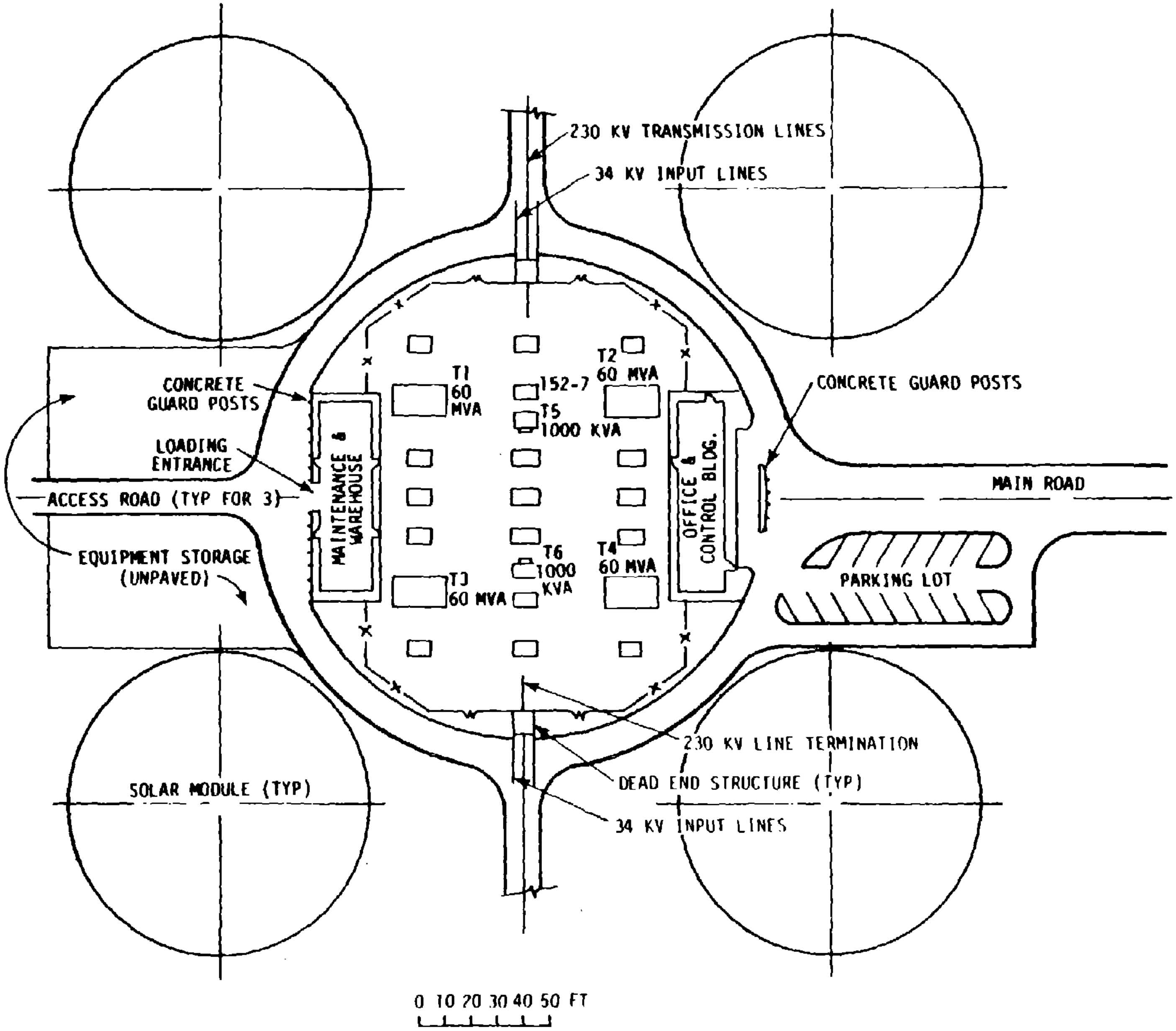


Figure 7-2. Switchyard and headquarters complex layout (Ref. 94)

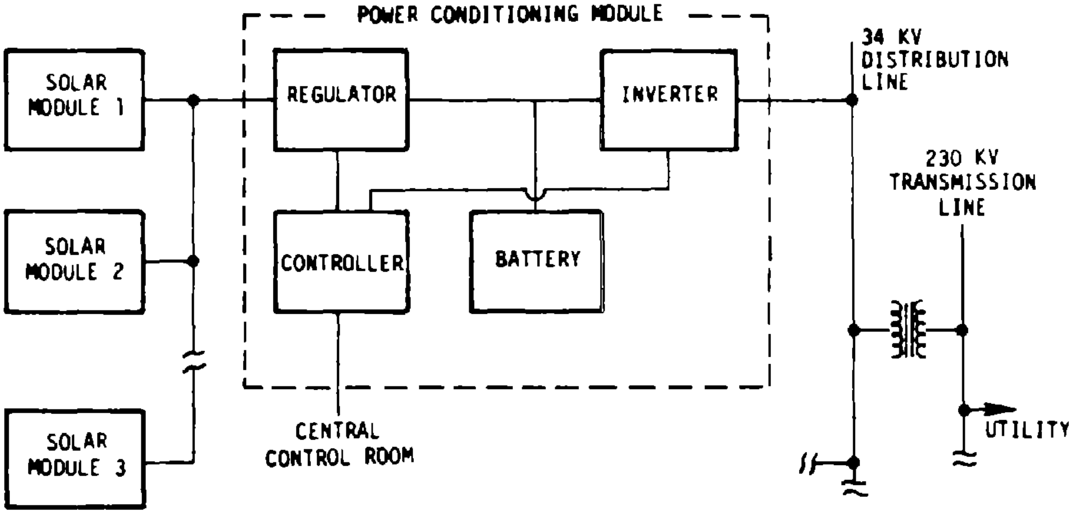


Figure 7-3. Block diagram of power conditioning module (Ref. 94)

6. Power supplied by the utility to charge battery.

7. Shutdown.

Depending on several factors including time of day, temperature, cloud cover, wind, and atmospheric conditions, the controller will be programmed to initiate one of the operational modes.

Energy storage may not be utilized in the first photovoltaic power systems constructed. According to one source, system studies have indicated that for load-center or central power station applications, onsite storage would not be cost effective (96). It is stated elsewhere, however, that if solar power is to contribute appreciable blocks of power to future utility networks, lack of energy storage will most likely be unacceptable (94).

Two types of batteries, lead-acid and lithium-sulfur, have been considered for energy storage for photovoltaic power systems. Lead-acid batteries do not appear promising for a number of reasons. Energy density is significantly lower in lead-acid batteries (11-22 Wh/kg) and thus a much greater mass of batteries would be required. Also the battery wastes lead, which could become less available in the future. High charging rates cause boiling and evolution of H_2, and high discharge rates cause electrode pitting. Lead-acid batteries are presently used in residential, industrial, and other small-scale photovoltaic power plants, since they are by far the most developed.

For the above reasons, it is believed that the total annual cost of the lithium-sulfur battery will be significantly lower than that of the lead-acid battery. The lithium-sulfur battery, developed by Argonne National Laboratory, will have an overall efficiency of approximately 80 percent (94). Its energy density is approximately 130 to 170 Wh/kg, and its lifetime is about 1000 cycles (7). The battery operates at a temperature of 450°C (840°F) and is insulated so that the exterior surface is only 32° (90°F). It is composed of about 6 percent lithium (as Li-Al and Li-Cl), with aluminum, potassium chloride, iron, sulfur, and boron nitride composing 1 to 2 percent. A battery fire would result in the release of Li_2O, SO_2, Al_2O_3, and various other pyrolysis products (94). The potential for occurrence of a cell fire is believed slight, since the battery will be contained within an iron cell casing that is further contained in submodules and insulated containers.

Other batteries in developmental stages are sodium-sulfur, nickel-zinc, zinc-chlorine, zinc-oxygen, and aluminum-air. The sodium-sulfur battery also appears attractive in that its energy density ranges from 170 to 200 Wh/kg and its lifetime is around

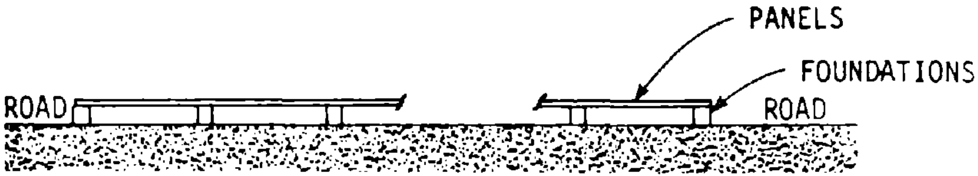
1000 cycles. The metal-air batteries are attractive because of low material costs and high energy densities, but there has been little progress in development of secondary air electrodes with long lifetimes (7). The nickel-zinc cell is hampered by the limited availability of nickel and the short lifetime of the zinc electrode (7). The zinc-chlorine system could be suitable for large-scale energy storage if suitable lifetimes can be obtained (7). Other types of energy storage systems being considered include pumped-hydro, compressed air, hydrogen, flywheel, and superconducting magnet systems (7). Batteries are still the most likely choice.

7.2 FLAT-PLATE INSTALLATIONS

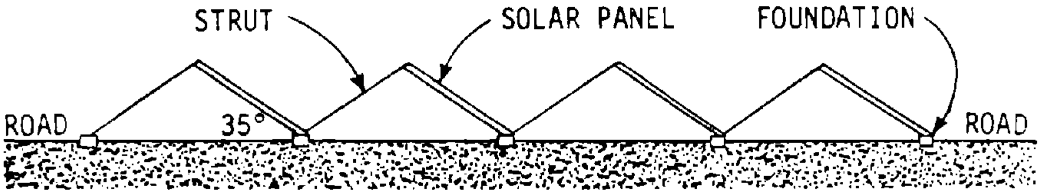
As mentioned earlier, the first photovoltaic central power stations will most likely be constructed with flat-plate arrays incorporating single-crystal silicon cells. Five array designs thought to represent the range of possibilities, shown in Figure 7-4, are as follows: (95)

- Horizontal Array - Panels are secured horizontally on precast concrete sleepers with a small slant angle to provide for drainage (Figure 7-4a).
- Tandem Array - Panels are supported on sawtooth-like structures with shared foundations. These are south-facing at a fixed tilt angle (Figure 7-4b).
- Augmented Array - This is the same as a tandem array with addition of reflector panels on the uncovered support struts. The solar panels are tilted at an angle 10 degrees steeper than the reflector panels (Figure 7-4c).
- Tilt Adjusted Array - This is a tandem array with tilt adjustment mechanisms that vary with changing sun angle (Figure 7-4d).
- East-West Tracking Array - Panels are mounted on a pedestal structure, which tracks the sun on a daily basis. Tilt angle is fixed (Figure 7-4c).

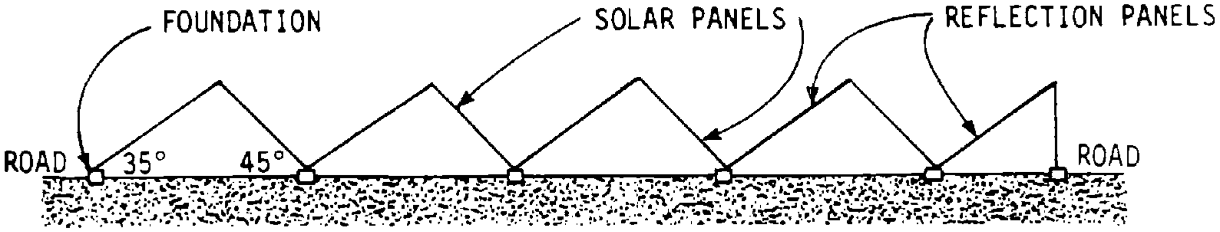
Several parameters are important in the performance and cost of flat-plate photovoltaic systems. Some of these include panel size, latitude siting, panel loading, ambient temperature (95), and actual load characteristics (93). Though larger panels will entail higher costs for the panel structure, the costs of the wiring, connection, handling, and field installation will be lower (95). Geographical location will also influence design and



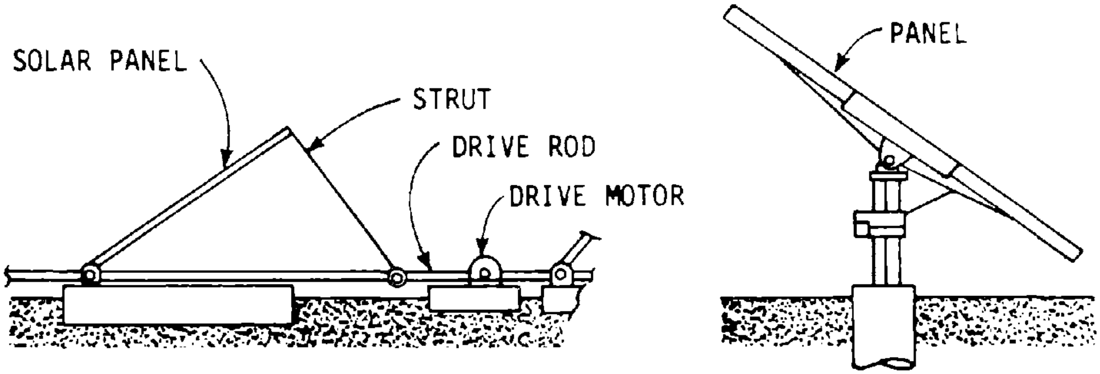
a. HORZONTAL ARRAY



b. TANDEM ARRAY



c. AUGMENTED ARRAY



d. TILT ADJUST ARRAY

e. TRACKING ARRAY

Figure 7-4. Side views of proposed flat-plate array designs (Ref. 95).

costs. Tilt angles of the panels must be adjusted as to specific site latitudes or to match output to seasonal load demand (95). As tilt angle increases, so do the requirements for land, road, wiring, and array structure. For photovoltaic systems with passive cooling, ambient temperature will also strongly affect the amount of energy generated, since at a given insolation level, the efficiency of a silicon solar cell is inversely proportional to cell operating temperature (95).

Although the basic costs of cells for flat-plate array systems are considerably lower than those of cells for concentrator systems, the flat plate array includes so many cost components that cost of the total installed system excluding cells comes close to the costs of an installed concentrator system, excluding cells. Because solar energy is of low intensity, the flat-plate system requires a large area for collection and conversion. Small amounts of electricity are dispersed over a large area, and extensive wiring is needed for interconnect. More extensive piping is also needed. The greater amounts of wiring and piping increase the installation costs.

7.3 CONCENTRATOR SYSTEMS

One approach to reducing the high costs of photovoltaic systems is to replace the high-cost cell area with lower-cost optical concentrator area. Concentrators focus sunlight on a cell area that is a fraction of the concentrator area on which the sunlight falls. Since the current from a photovoltaic cell increases almost linearly with increasing intensity of sunlight and voltage increases slightly faster than the log of the intensity, the use of concentrator systems can increase the power output per unit cell area (4). Higher current densities would occur with an increase in sunlight intensity and lead to resistive losses. These losses, however, can be reduced to make concentrator cells cost-effective. To make concentrator photovoltaic power systems feasible, not only must a high cell efficiency be maintained, but a high optics transmission (or reflection) efficiency and a low structure cost per unit area must be realized (97).

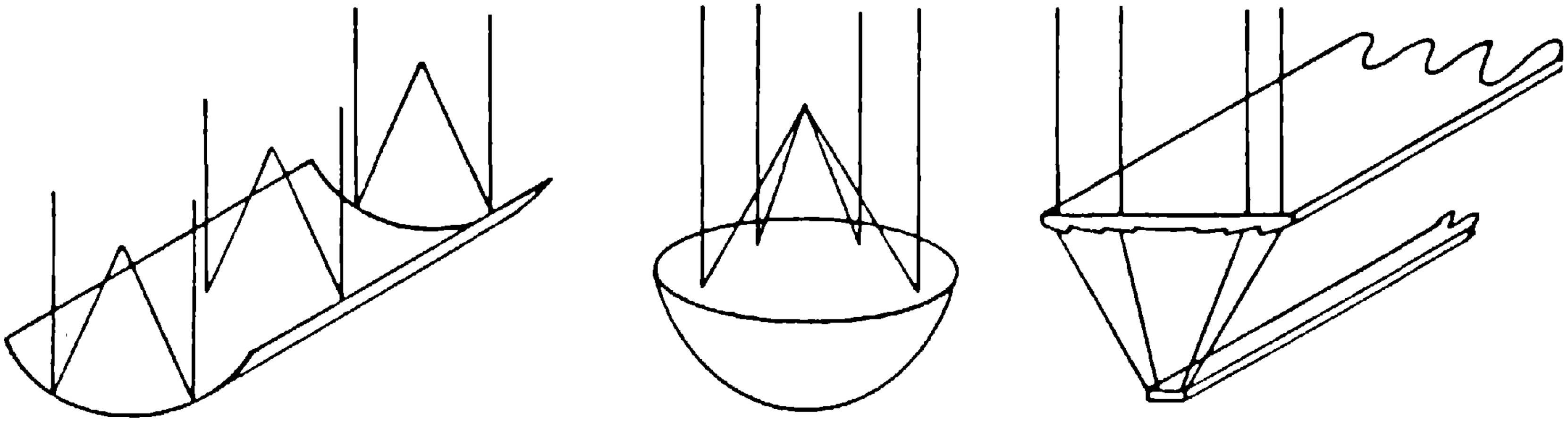
Three basic types of concentrating systems are being constructed: low (2-10x), medium (10-100x), and high (100-200x). Low concentrators are being studied for use with low-cost sheet or ribbon silicon cells (130), but may also be used with single-crystal silicon cells. Medium concentrators are being used primarily with single-crystal silicon cells and at present are the most likely candidates for commercial applications. High concentrators are being developed for use with compound semiconductor cells (primarily GaAlAs) and high-efficiency silicon cells (98). High-efficiency silicon cells are being used in most designs.

Several concentrating optics considered for use in photovoltaic systems are shown in Figure 7-5. The following discussion describes the various concentrators in terms of the type of concentrating optics used.

A concentrator using reflecting parabolic cylinders similar to that shown in Figure 7-5a is shown in Figure 7-6 with components. This concentrator has a concentration ratio of 200/1 and can generate 10 kW of power. This type of concentrator uses densely packed high-efficiency silicon cells, but could also use GaAs cells. The parabolic reflectors in the above design are glass mirrors. The system employs a two-axis tracking system and also a water-cooled photovoltaic receiver system that can supply thermal energy for heating, cooling, or industrial use (99). Two other photovoltaic concentrator designs are based on the reflecting paraboloid design shown in Figure 7-5b (100,101). These are shown in Figure 7-7. The concentrator in Figure 7-7a was constructed with an aluminized polyester film (DuPont's Mylar D) as the reflector surface (100). The shape of the reflective surface is maintained by a vacuum in back of the surface. The concentrator is totally enclosed within an air-infiltrated plastic bubble for protection against wind and weather. Concentration ratios will range from 100 to 200 suns. Initially Tedlar was to be used for the enclosure, but the cost was prohibitive. Recently substitutes for Tedlar, costing only 10 to 20 percent as much, have been identified. Tests performed recently indicate that this type of reflector has an optical efficiency of 83 percent (98).

The concentrator shown in Figure 7-7b is to be based on the design and construction of an automobile headlight (101). Like the headlight, the proposed concentrator will consist of two glass halves: one a reflector with a metallized reflective surface (aluminum), and the other a clear glass cover. The solar cell is mounted on a liquid-cooled substrate fused into the glassware. The two glass halves are fused together and the inside filled with an inert gas such as argon. Concentration ratios from 100 to 500 suns intensity may be attained with this design.

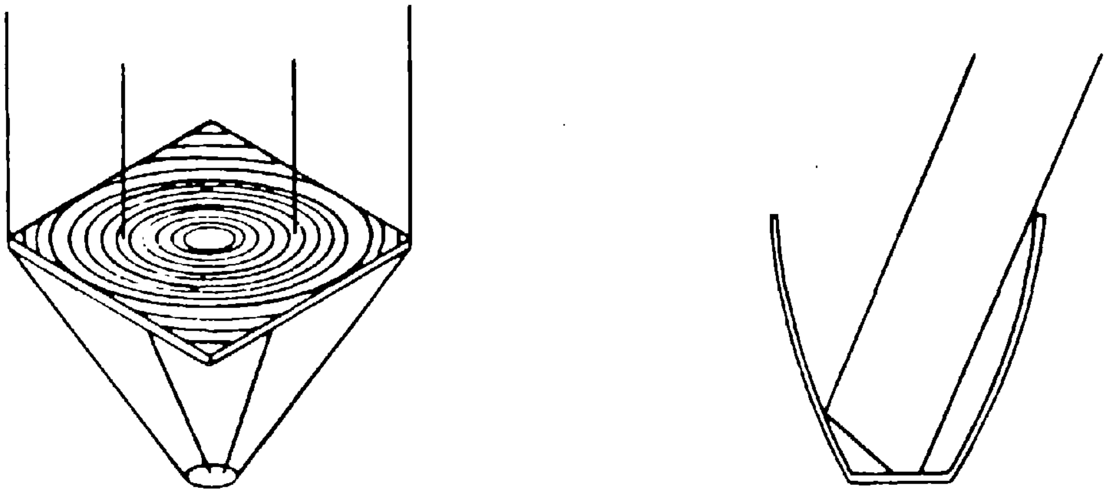
A variety of photovoltaic concentrating systems have been produced using Fresnel lenses. These lenses are usually made from optical-quality acrylic plastic such as polymethylmethacrylate. Three types of Fresnel lenses are shown in Figure 7-8. Most such concentrating systems have used Fresnel lenses of the grooves-down type. With the grooves-down Fresnel lenses transmission losses are fewer and cleaning is easier because the smooth side of the lens faces outward. The domed Fresnel lenses provide more transmission, mechanical strength, and rigidity than the other lens types (97). The domed lens also yields much higher concentrations (up to 1700 suns was reported), and potentially can reduce the costs of high concentration systems to near those of moderate concentration systems (97).



a) REFLECTING PARABOLIC CYLINDER

b) REFLECTING PARABOLOID

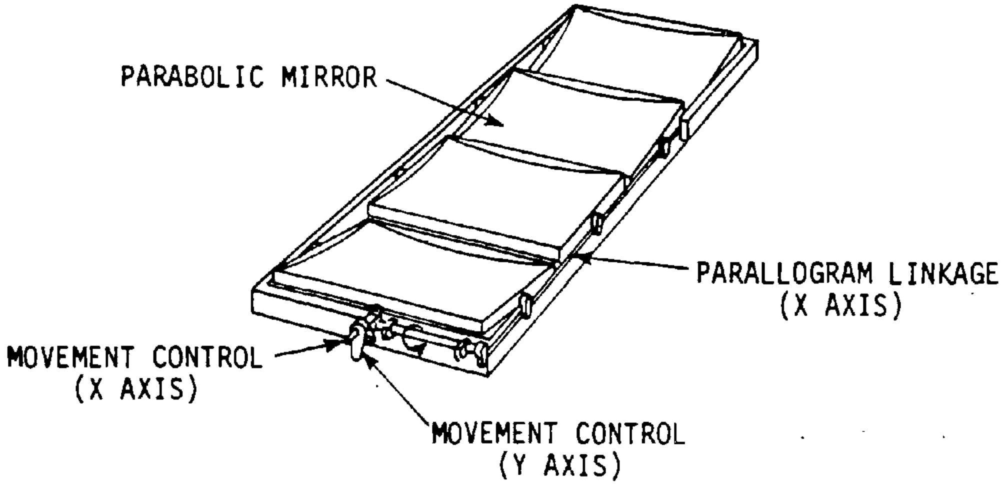
c) REFRACTING CYLINDRICAL FRESNEL LENS



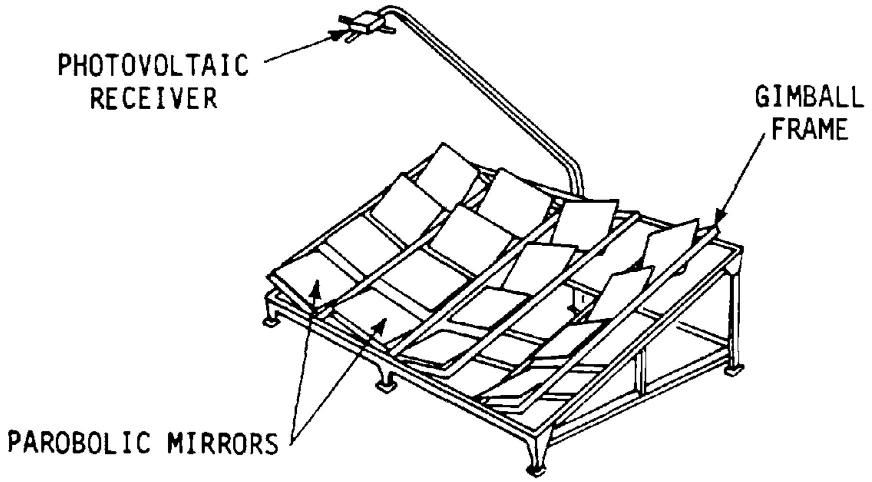
d) REFRACTING SPHERICAL FRESNEL LENS

e) REFLECTING COMPOUND PARABOLIC CONCENTRATOR

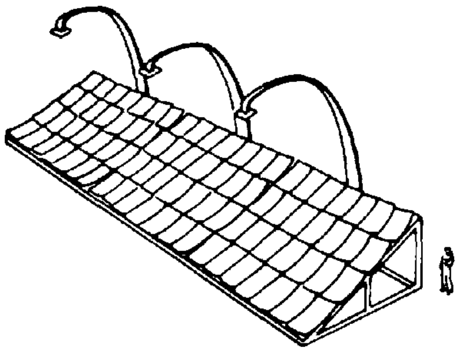
Figure 7-5. Various types of concentrating optics under consideration for photovoltaic applications (Ref. 90)



a. Gimbal frame with reflectors.

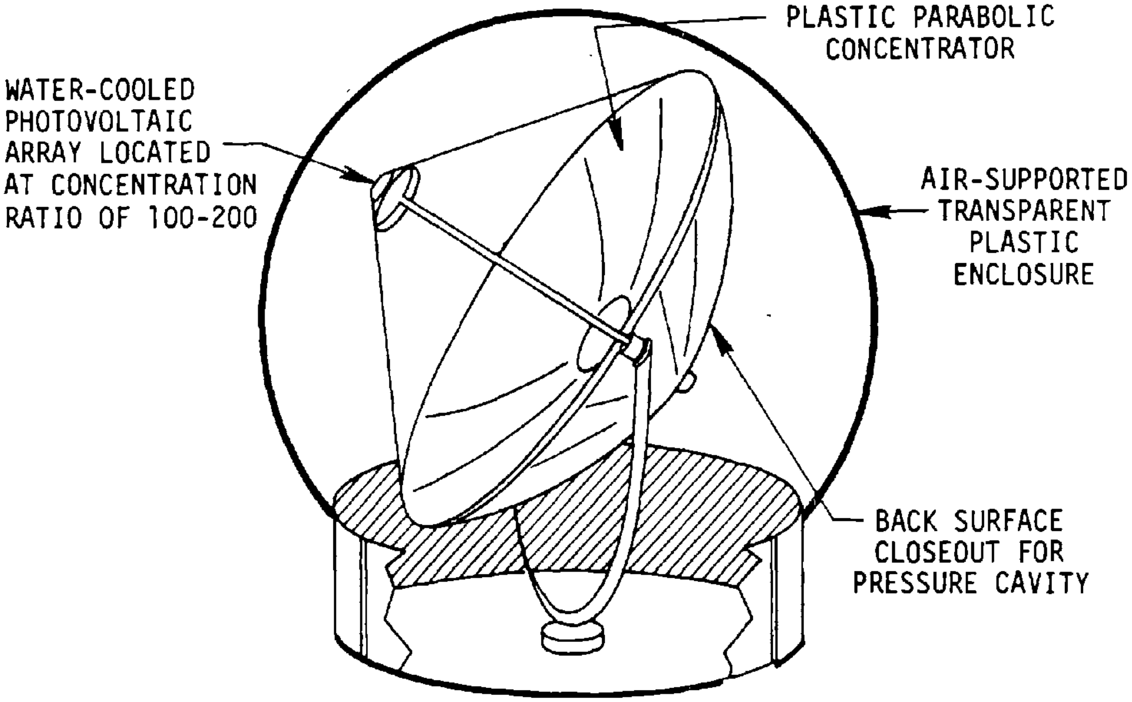


b. Photovoltaic 200/1 concentrating collector module.

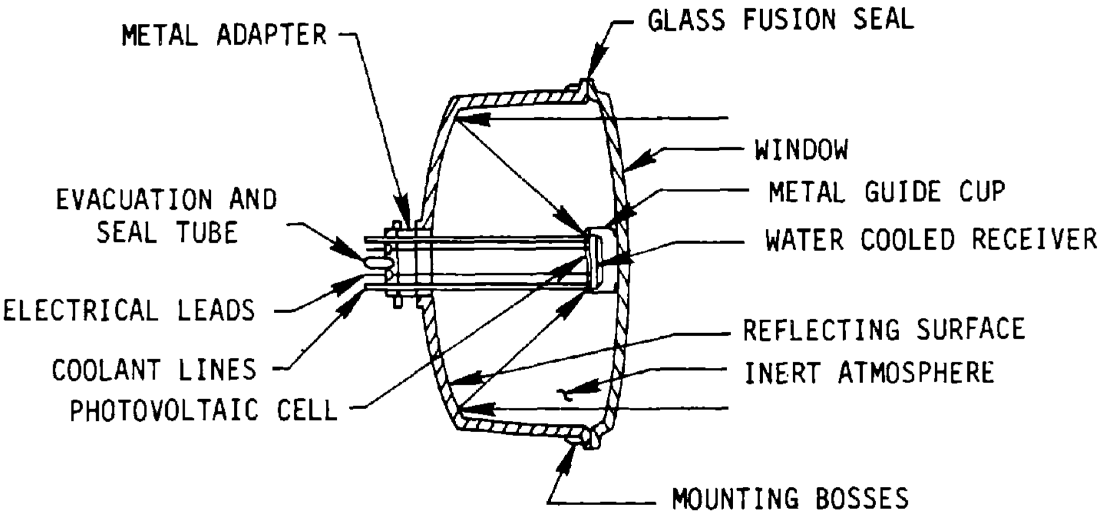


c. 10 kW array.

Figure 7-6. Photovoltaic concentrator systems using parabolic reflecting mirrors (Ref. 99)



a. Concentrating photovoltaic system concept (Ref. 100)



b. Headlight concentrator design (Ref. 101)

Figure 7-7. Photovoltaic concentrators using a parallel structure

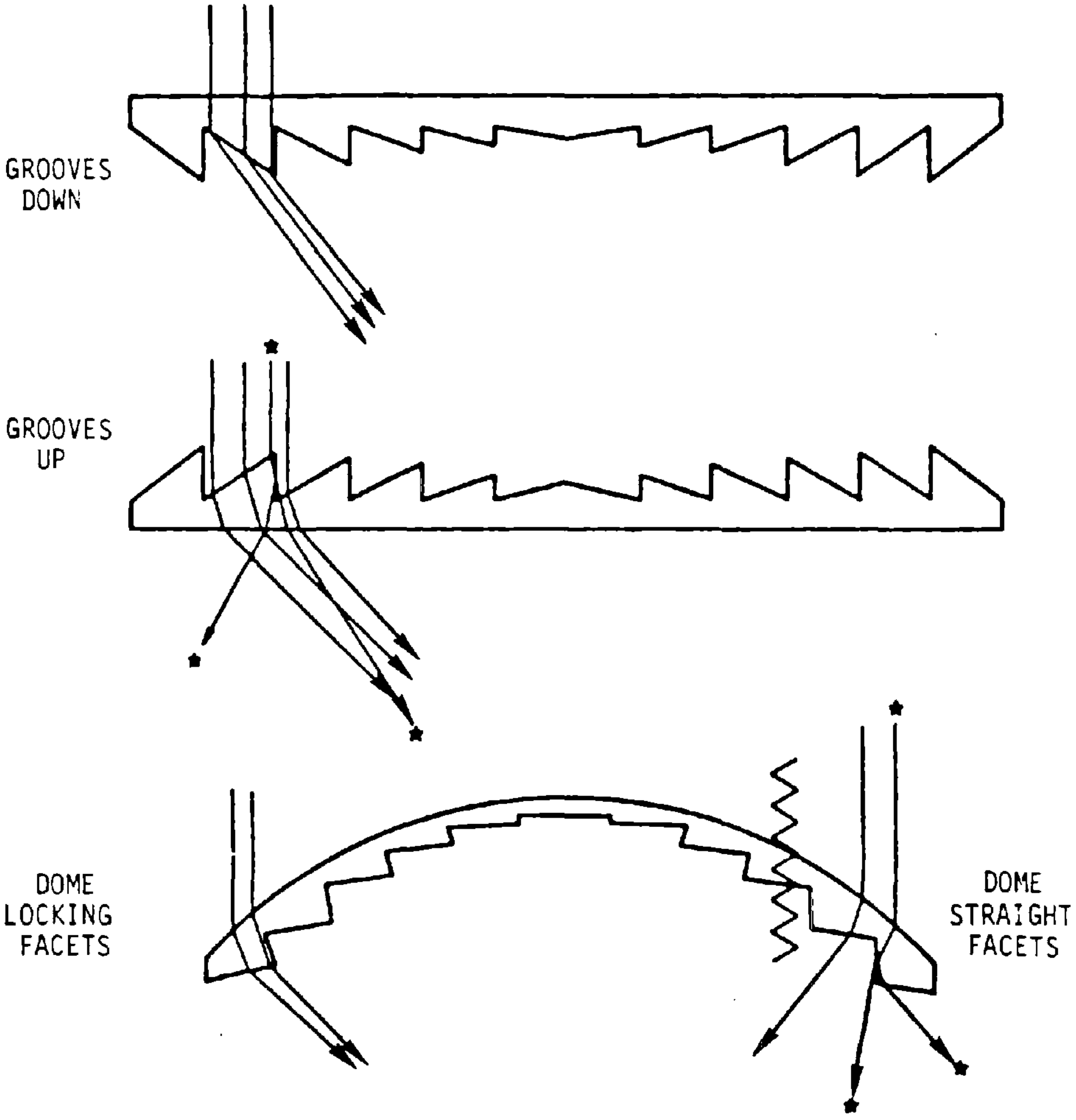
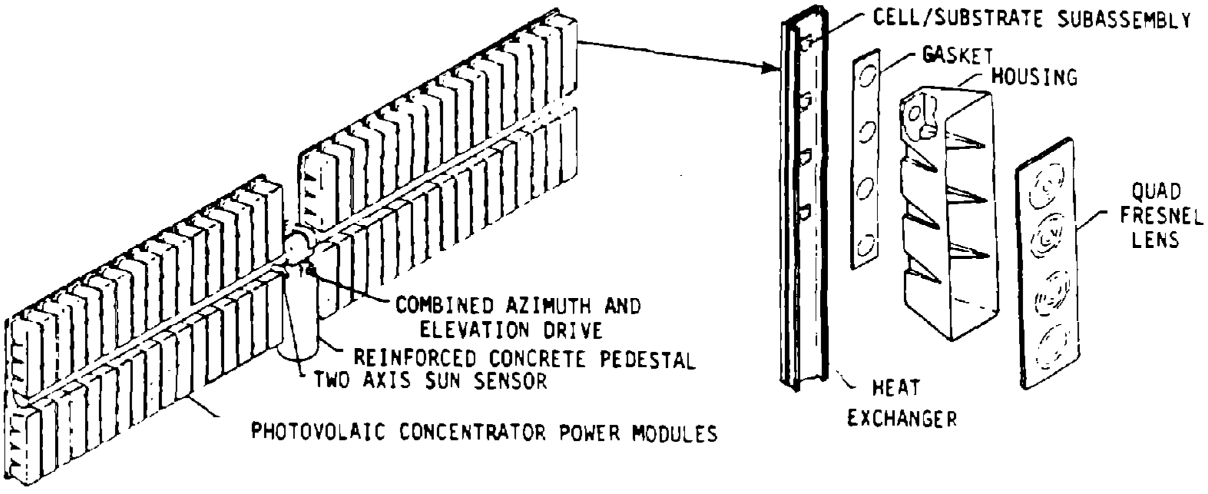


Figure 7-8. Three types of Fresnel lens. Facets are shown greatly exaggerated (Ref.97)

Two proposed photovoltaic concentrating arrays using Fresnel lenses are shown in Figure 7-9 along with their components (102,103). The array in Figure 7-9a consists of 68 detachable modules (272 solar cells) mounted on a horizontal support tube (102). The concentration ratio is 40 suns. A two-axis tracking system is passively cooled and delivers 2.27 kW at peak power (9.0 percent efficiency). The array in Figure 7-9c consists of 36 modules (144 solar cells) with a lens area of 7.2 x 3.2 m^2 (103). The array also has a two-axis tracking system and is passively cooled by means of an aluminum beam with cooling fins. It gives a practical concentration of 60 suns with the Fresnel lens. In both of the above arrays the Fresnel lens will be an integral part of the cell enclosure and thus provide cell protection. These designs will eliminate the need for solar cell cleaning, will make possible automated cleaning of the concentrator lens surface, will protect against accidental burns or eye damage since the cell is enclosed, and will protect against vandalism since the acrylic material can tolerate hand-thrown rocks.

A compound parabolic concentrator (CPC) like that shown in Figure 7-10 is a type of low-concentration device being investigated. Also being investigated is the dielectric compound parabolic concentrator, (DCPC). The DCPC uses a dielectric and operates by total internal reflection. The proposed module shown in Figure 7-10b utilizes DCPC's as secondary concentrators (94). Both of these concentrator designs are being developed by Argonne National Laboratories. The basic CPC concentrator elements are injection-molded from acrylonitrite-butadiene-styrene copolymer (ABS) (98). The CPC substrates are then treated with an undercoat polymer, evaporated aluminum, and a protective overcoat. The basic DCPC concentrator elements are injection-molded polymethylmethacrylate (98). These are low-concentration devices with a concentration ratio of about 10 suns. They may be used as primary or secondary concentrators.

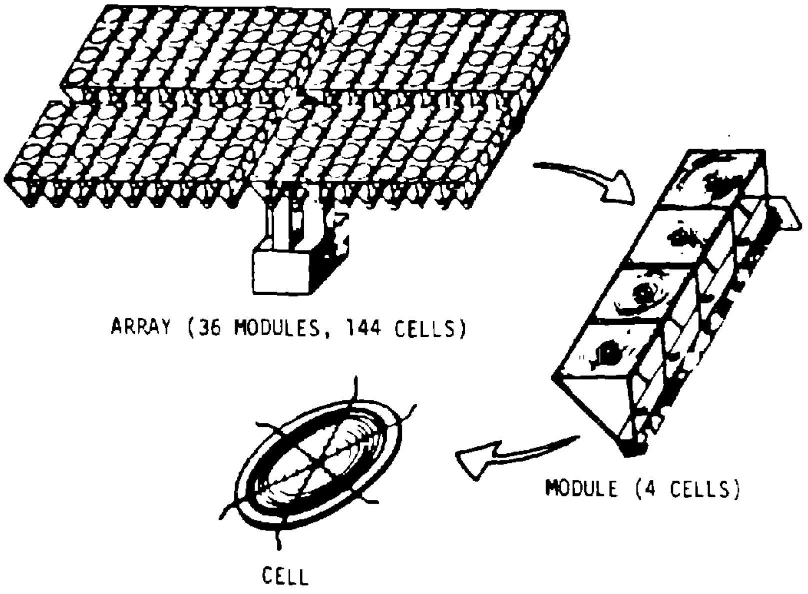
Two novel concentrators have been proposed, one using fluorescent materials such as rare-earth-doped glass or plastic doped with dyes and one using organic laser dyes contained within a plexiglass box (104,105). Diagrams of these two concentrators are shown in Figure 7-11. The principle of the fluorescent (or luminescent) concentrator is that light of various wavelengths is absorbed by the dopants or dyes and is emitted as luminescence. If solar cells are placed around the edges of a plate or box doped or filled with fluorescent materials, the light is emitted and used by the solar cell. Some advantages of using concentrator cells of this type would be (1) relatively high efficiency on cloudy days, since high-efficiency collection of diffuse light can be achieved; (2) high concentration ratios with tracking of the sun; (3) reduced heat dissipation problems; and (4) capability



a. Photovoltaic concentrator arrav (PCA). The PCA is 9 ft. high by 42 ft. lonq.

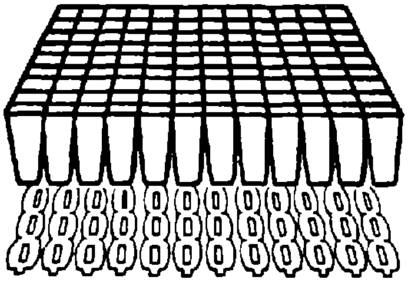
b. Four cell module.

(Ref. 102)

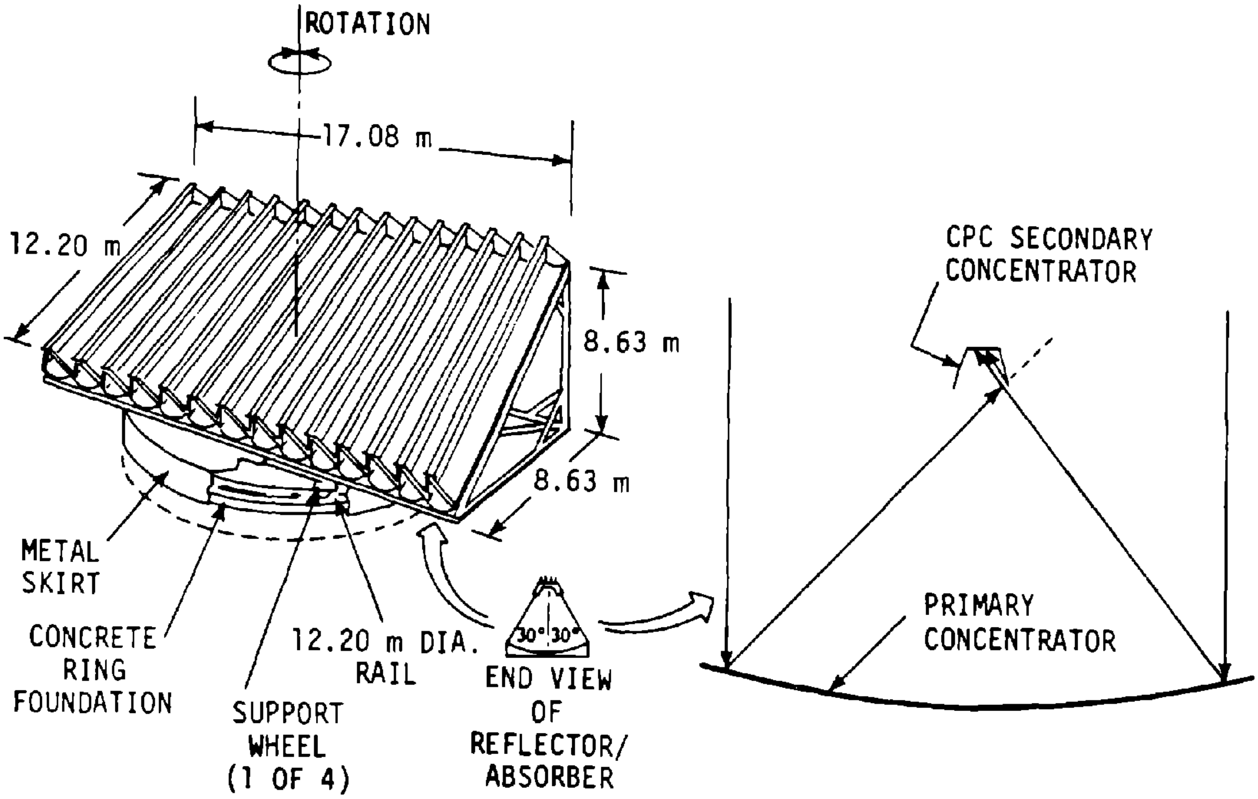


c. Array, module, and cell (Ref. 103)

Figure 7-9. Arrays utilizing Fresnel concentrators

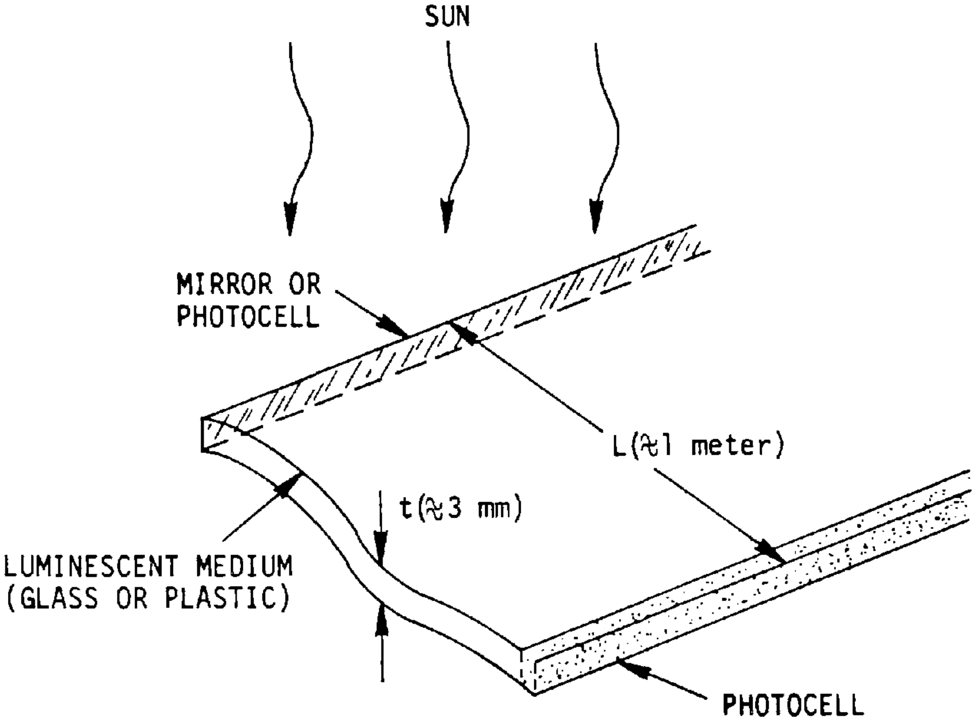


a. Acrylic CPC developed by Argonne National Laboratory (Ref. 66)

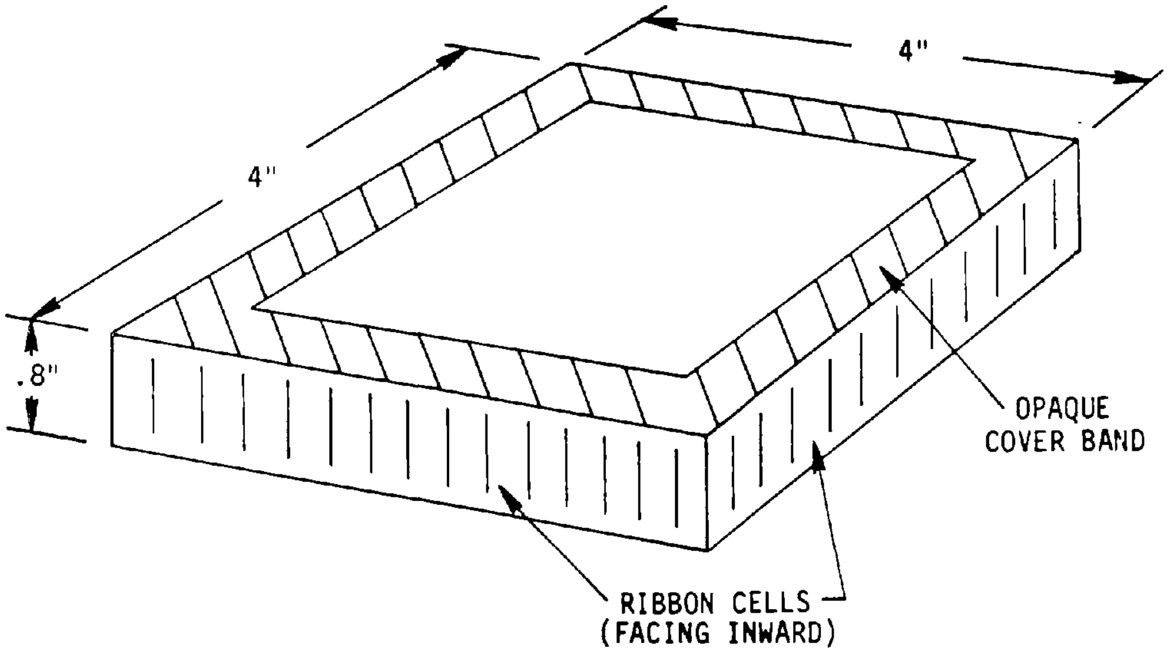


b. 26 kW solar module concept. (Ref. 94)

Figure 7-10. Compound parabolic concentrators used as primary concentrator (a), and secondary concentrator (b,c)



a. Schematic of proposed concentrator using luminescent material-doped medium (Ref. 104)



b. Proposed concentrator using fluorescent organic laser dyes (Ref. 105)

Figure 7-11. Proposed luminescent concentrators for mass production by available techniques (104). Results with the concentrator shown in Figure 7-11a showed 2.3 percent collector efficiency, assuming 20 percent efficiency of the silicon cell. Use of gallium arsenide cells can significantly increase the collector efficiencies (104). The collector plate is acrylic, covered with acrylic film doped with an organic dye, Coumarin 6.

The interior of the box shown in Figure 7-11b was filled with four organic laser dyes dissolved in ethanol: Coumarin 481, Coumarin 540, Rhodamine 590, and Rhodamine 640 (105). The output of this cell was 84 percent of that expected. One problem with using the dyes, however, is their short lifetimes; in outdoor tests all dyes had faded completely within 5 days.

7.4 SAFETY AND INDUSTRIAL HYGIENE CONCERNS AT PHOTOVOLTAIC INSTALLATIONS

The hazards potentially associated with photovoltaic installations are of four basic categories:

1. Electrical hazards.
2. Fire hazards (including explosions).
3. Optical hazards.
4. Miscellaneous hazards. This includes typical hazards associated with maintenance, construction, and operation of electromechanical equipment.

7.4.1 Electrical Hazards

The most prominent potential hazard in a photovoltaics power station is electrical shock. Current flow, which is dependent on the voltage and resistance, is the factor that causes injury in electric shock (106). Death or injury by electric shock may result from several effects of current on the body (106).

In photovoltaic systems, a direct current will be involved prior to tie-in with the inverter. Relative to alternating current (at commercial frequency of 60 H_z), a direct current requires a larger amount of current flow to inflict a similar injury. As an example, it is estimated that 100 mA at 60 H_z may cause ventricular fibrillation, whereas with direct current, 500 mA is required to initiate ventricular fibrillation. This amount of current could be easily obtained from one array string.

Safety precautions should be taken to prevent contact with components that could produce serious electrical shock. Although higher operating voltages reduce transmission losses, they increase the chances of serious electrical injury. Efforts are being made to limit operating voltages in residential and industrial applications to 200 to 250 V. Higher voltages (1500-2000 V) apparently will be limited to the utility industry by building code restrictions. Various interconnect configurations for modules can be used to reduce output voltage, such as reducing the numbers of cells and/or modules connected in a series. All modules should be properly insulated and grounded. For systems operating at 200 to 500 V, insulation and grounding for 1500 dc volts are recommended.

At one test facility the solar cell panel mounting frames are connected to an array field ground through a network of buried copper cable and ground rods (107). This arrangement is to provide personnel safety and to limit damage from lightning. Isolation transformers are also recommended to protect against lightning (108). It is anticipated that in the event of a direct strike, with grounding and arresters, only one panel out of an array would be damaged.

At the test facility mentioned above, each series string is connected to the solar array busbars through disconnect switches (107). For maintenance or repair of a panel within the series of strings, the switches are opened and should be locked out. Array dc wiring can also be isolated from control room dc wiring with a master switch, which can be opened and tagged to allow work on the control room wiring. Also at the same test facility the array was connected to the busbars in the control room through a switch, an insolation diode, and a fuse (107). It was noted elsewhere, however, that since dc systems are current-limited, fault-sensing breakers should be used rather than fuses or circuit breakers (108). Fault-sensing breakers are sensitive to very low levels of current leakage to ground and are designed to limit the electric shock to values of current and time duration below those that can produce serious injury.

Work involving physical contact with an array should preferably be performed at night when the array is not producing power. Work may be performed during the daytime by use of isolating switches such as those described above and by shorting output terminals of the panels (107).

Barriers to prevent accidental contact with electrical equipment are also suggested. Fences should be placed around critical areas. Warning signs should also be displayed in all hazardous areas, including high-voltage areas and exposed current-carrying parts (106).

7.4.2 Fire and Explosion Hazards

Other potential hazards are fire and explosion. Fires would most likely occur in installations where cells are densely packed and high temperatures and flammable materials are more prominent. Because of the high concentrations involved, overheating could easily occur, if, for example, the cell cooling system malfunctions. Some of the concentrators being designed for high-concentrator systems use the Fresnel lens, usually composed of methyl methacrylate, which is very flammable. A serious fire possibly could spread throughout a photovoltaic installation by way of the Fresnel lens.

In field tests of silicon cell modules many of the cells overheated to such an extent that modules were discolored, burned, or charred, and solder remelted (109). A possible cause of the overheating was reverse biasing due to shadowing, fracturing, or power degradation of the cells. Another possible cause was faulty interconnects. In one test, cutting an interconnect wire resulted in arcing, smoking, and occasional flames.

The flammability of most materials used in silicon cell fabrication is low or moderate. Some materials, however, including polyvinylbutyryl (PVB), polyvinyl chloride (PVC), and ethyl vinyl acetate (EVA), which are candidate materials for pottants and adhesives, may release their constituent monomers upon thermal degradation. Because these monomers are highly flammable when exposed to heat or flames (110), it is possible, though unlikely, that a widespread fire could occur. Any fire would most likely be confined to one modular unit. Although the failures described above occurred with silicon cells, it is possible that such failures could also occur in cells of cadmium sulfide, gallium arsenide, or the various other substances being developed.

Assessing completely the potential for fire at an installation would necessitate a complete inventory of materials and their flammability. Preventive measures for limiting the outbreak and spread of fires include (111):

- Flammability testing of materials used in solar units, and other site structures prior to selection and use.
- Design criteria for circuit configuration and component selection.
- Devices for detecting a failure that could lead to a fire.
- Adequate numbers and kinds of extinguishers at proper locations.

- Use of automatic or passive firefighting systems.
- Well-developed and well-practiced emergency procedures.
- Component separation and size limitation.

The use of lead-acid batteries for energy storage in photovoltaic systems will probably be a major potential source of explosion hazards. Care must be taken when charging the batteries to prevent the rapid generation of hydrogen, which is extremely explosive. The building used for storing batteries should be designed to handle batteries and well ventilated to handle flammable gases.

7.4.3 Optical Hazards

Another potential occupational hazard is the possibility that operators may enter the path of concentrated sunlight from concentrator systems. Concentrator systems using reflectors with long focal lengths, such as parabolic trough or dish systems, pose a greater hazard than do systems using concentrators with relatively short focal lengths, such as the Fresnel lens. In certain orientations the trough lens focus can extend beyond one end of the trough or dish, possibly causing a serious potential hazard. In normal concentrator operation, however, it would be difficult for someone to enter the path of the lens focal point. At distances greater than one focal length, the possibility of injury is slight since the light is diffuse. With most concentrator designs using Fresnel lenses it would also be difficult to enter the path of the focused light. Even so, the installers of both types of systems should be aware of the potential hazard. Warping could possibly shift focal points and thus potentially cause injury to operating or maintenance personnel.

To prevent injuries, parabolic trough systems should be fenced in to prevent entrance of persons other than plant personnel. During maintenance or repair the trough system should be defocused. To prevent warping of Fresnel lenses, designers are considering changes in the annualing cycle of the lens or doming of the lens.

Since light energy reaching the retina of the eye is converted into heat, thermal damage (chorioretinal burn) to the eye is also a possibility (112). Because of the poor heat-removal mechanism of the retina, a short exposure to a large amount of radiant energy could cause chorioretinal burn. Retinal hazard thresholds depend strongly on image size for momentary viewing (i.e., 0.15 to several seconds). Calculations have shown that in most cases exposure of personnel who are not near the focus and/or alignment point for more than blink-response exposure (i.e., about 0.15 s) does not present a high risk for biological damage and normally would not be any worse than a direct glance at the sun. Eye damage could occur, however, if a person is exposed near the focal point. To prevent this, workers should wear goggles with side shields at all times during inspection and maintenance of concentrator systems.

7.4.4 Miscellaneous Hazards

Various other hazards less likely or of a less serious nature than those discussed above may also occur at photovoltaic installations. These are discussed briefly below.

Hazardous Materials--

Only under extreme conditions, such as in the event of a fire, would there be any need for concern regarding toxic chemicals at a photovoltaic power installation. Probably the most serious problem would be a fire at a photovoltaics installation utilizing GaAs cells. If the fire involved a large portion of the cells, significant quantities of As_2O_3 could be formed (8). Health effects of As_2O_3 are discussed in Section 8.3.2. Although less likely, a fire at an installation utilizing CdS cells could result in volatilization of the CdS and thus create a hazard to workers. Health effects of cadmium are discussed in Section 8.2.1. A fire could also lead to release of the monomers of pottants or adhesives such as PVC, EVA or acrylic, which are highly toxic.

Even though a fire may result in release of some toxic materials, it is unlikely that significant amounts would be released or that personnel would be exposed to significant concentrations, since the installations are out-of-doors and emissions would be readily diluted. Fires would probably be confined to single module units. In the event of a fire in one module, personnel extinguishing the fire should be equipped with the proper protective clothing and respiratory apparatus. The use of automatic fire extinguishing systems is preferable.

Electromagnetic Interference--

Potential electromagnetic interferences from photovoltaic power plants could cause interferences with communication equipment of aircraft. Since, however, the interferences are of low level and frequency, the effect should be small. Tests should be developed to determine the possibility of electromagnetic interference of a photovoltaic system with pyrotechnic devices (blasting equipment) and medical devices (pacemakers) (111).

Hot Surfaces--

Provisions should be made in the design of photovoltaic systems to protect persons from inadvertently touching hot surfaces. In concentrator systems that need active cooling, the hot surfaces of photovoltaic receivers and hot fluid loops that could be contacted should be covered, screened, or insulated. Again, fences could help prevent access to modules by unqualified personnel. The unit should be allowed to cool before it is serviced.

8. TOXICOLOGICAL EVALUATION OF MATERIALS USED IN PHOTOVOLTAICS PRODUCTION

The anticipated increase in production of photovoltaic cells and related base materials will necessitate an increase in workers for these industries. The expected increases in output and in number of workers warrant an evaluation of the potential occupational and health hazards of this industry.

This section is a toxicological evaluation of those materials noted in Sections 3 through 6 that are used in the manufacture of photovoltaic cells and related components. Since present efforts are directed primarily toward cells made of silicon, cadmium sulfide, and gallium arsenide, the materials used in production of these three cell types are the primary focus of this section. Materials used in other types of photovoltaic cells now in developmental stages are also considered, as are materials associated with installation components.

8.1 POTENTIAL HAZARDS IN PRODUCTION OF SILICON CELLS

Production of silicon cells involves the mining of quartz, refining of the quartz to silicon metal, purification of the silicon to a solar cell grade, recrystallization, doping, grid placement, cell assembly, and encapsulation. Occupational and health hazards in each of these production phases are discussed in the following sections.

8.1.1 Production of Solar-Grade Silicon

Exposure to crystalline silica is a primary health threat to workers involved in the mining and refining of the raw quartz for solar-grade silicon. Workers who load, unload, and clean the electric arc furnaces used to reduce the quartzite may be exposed to SiO_2.

Exposure to crystalline SiO_2 may lead to a condition known as silicosis. Symptoms associated with silicosis are cough, dyspnea, wheezing, and various chest illnesses. These symptoms may progress with continued exposure to SiO_2. Epidemiological studies on silicosis are discussed elsewhere (113). Exposure to silica has been found responsible, in at least one case, for massive proteinurea (presence of protein in the urine) and acute renal failure (114).

It is important that a differentiation be made among the different forms of silicon that may be encountered in production of silicon cells, especially among crystalline silica, amorphous silica, and silicon metal. As noted above, crystalline silica (SiO_2) occurs in nature and is mined, usually in the form of quartz. Health hazards associated with exposure to crystalline silica are well covered in the literature. Amorphous silica (noncrystalline) is also found in nature as diatomaceous earth, or diamotite. Amorphous silica may also be formed in the production of MG-Si from quartz or upon decomposition of silanes or chlorosilanes. Silicosis has been induced in animals by intratrachial injection of diatomaceous earth, and diatomite workers show evidence of silicosis (117). In surveys by Plunkett and DeWitt (119), and Volk (120) of commercial amorphous silica workers, no evidence of pneumoconiosis was found with 8 to 12 years of exposure. In another study of 165 workers exposed to precipitated amorphous silica (PAS), no relationship was found between pulmonary function testing parameters or chest radiograph findings and either the quantity of or duration of exposure to PAS (121).

Workers at a plant producing MG-Si by electric arc furnace reduction were studied for exposure to amorphous silica (121). The amorphous silica was produced when vaporized silica escaped through stacks or into the work areas, condensing to form a fine powder. It is estimated that 12 to 14 tons per day of vaporized silica escaped into the work area or through the stacks.

Because of the roetgenographic changes noted in these 11 analyses, NIOSH undertook a controlled study of laboratory animals to establish a TLV and evaluate the pathologic responses, primarily pulmonary fibrosis (122). The results showed that these amorphous dust samples had the potential for inducing fibrogenic pulmonary response following inhalation of sufficient quantities of material (122).

It is doubtful that amorphous silicon poses a serious health threat in the photovoltaics industry. In the event that large quantities of silane, chlorosilanes, or fluorosilicates are released, the primary hazard would be exposure to HCl or HF rather than to the small amount of amorphous silicon that might form. It is possible, however, that significant quantities of amorphous silicon can be released during quartz reduction in an arc furnace. It is suggested that concentrations in workplace air be kept below 20 million particles per cubic foot (mppcf) until additional data on biological activity become available (117).

The current OSHA standards :

$$\text{TLV} = \frac{<50}{\%\ \text{quartz} + 5}\ \text{mmppcf}$$

The second formula is for the TLV of respirable dust by the mass method:

$$\text{TLV} = \frac{10}{\%\ \text{respirable quartz} + 2}\ \mu g/m^3$$

where respirable dust is defined as dust with an aerodynamic diameter less than 5 μm (123).

The environmental exposure limit recommended by NIOSH is 50 $\mu g/m^3$ (123).

Silicon metal does not occur naturally, and little information is available on possible consequences of inhaling silicon dust. Because of the future increase in silicon solar cell production, more information is needed on possible hazards of silicon metal dust. Metallurgical-grade silicon in chunk or powder form may be transported and handled extensively for use in production of solar-grade silicon. These activities could result in significant fugitive dust levels and worker exposures. A short-term exposure limit of 20 mg/m^3 has been tentatively established for silicon (117).

Giles et al. reported the presence of 264 ppm silicon in the kidney of a male sandblaster who died from kidney failure. Since no primary or systemic causes of renal disease were found, renal failure was attributed to acute renal silicon toxicity due to the abnormally high silicon content (114). It should be noted that the sandblaster probably was exposed to crystalline silica, although the authors describe the exposure as being to silicon. Even though the mode of entry of silicon was in the form of silica, it is difficult to determine from this paper whether silicon or silica was responsible for the observed renal dysfunction. This same lack of differentiation between silicon and silica is apparent also in the study by Saldanha et al., who found that elevated silicon content in the kidneys of a male bricklayer was responsible for a distinct nephropathy, characterized by proteinuria and arterial hypertension (115).

It is believed that the cause for endemic nephropathy, found only in specific locations in the Balkans, is the high silicon (in the form of silica) content of the water in these areas (116). Here again it is not clear whether silica or silicon is responsible.

Reduction of the SiO_2 in the arc furnace results in the formation of silicon and also of silicon monoxide (SiO), silicon carbide (SiC), and carbon monoxide (CO). Upon exit from the furnace the CO gas stream carries with it silicon, SiO, and SiO_2 fines, as well as combinations of these fines. Most of these are filtered out in the dust collection system. Workers could be exposed to silicon, SiO, and SiO_2 particulates during cleaning or replacement of the filters in the dust collection system. Also, any defects in the duct system removing the CO could result in CO, SiO, SiO_2, and silicon in the work environment. Silicon monoxide in the condensed phase is believed to consist of silicon and SiO_2 in a 1:1 mixture unless it is rapidly dry-quenched (8). Pure SiO exists as a gas (8). It is believed that the Si-SiO from the arc furnace is oxidized to SiO_2 upon contact with air (8). The exact nature of the dust in the CO gas stream has not yet been defined. In any case, there is potential for exposure to crystalline SiO_2, amorphous SiO_2, and fused SiO_2 at this phase of production. Possible health effects from exposure to SiO plus silicon from the arc furnace are not known. The structure and composition of this SiO dust should be determined in greater detail.

The acute effect of CO is asphyxia. Since CO is much more soluble in hemoglobin than oxygen, it combines with the hemoglobin, depriving the tissues of oxygen. Some chronic effects as a result of repeated low-level exposures include heart irregularities, hearing disturbances, contraction of the visual fields, and glycosurea (high sugar levels in the urine) (42,124,127). The current OSHA standard is 50 ppm for an 8 hour time weighted expsoure (TWA). NIOSH has recommended a 40 mg/m^3 (35 ppm) TWA and a 229 mg/m^3 (200 ppm) ceiling limit (123).

After reduction of the quartz the molten silicon is drawn off, allowed to crystallize, and then milled. Unless the mill is enclosed and equipped with an exhaust system, workers may be exposed to the silicon dust generated during milling. As mentioned above, information concerning exposure to silicon metal dust is scarce, although silicon has been referred to as a cause of renal abnormalities (117,128,129).

8.1.2 Purification of Silicon

The powdered MG-Si is next fluidized and allowed to react with hydrochloric acid (HCl). This reaction results in the formation of hydrogen and mono-, di-, tri-, and tetra chlorosilanes. At least one company produces chlorosilanes by reaction with methyl chloride to form intermediate methyl chlorosilanes, from which the chlorosilanes are produced (130). As discussed above, three major process alternatives are presently being developed to reduce costs of SeG-Si silicon. Presently silicon ingots are formed primarily from tetrachlorosilane ($SiCl_4$) and trichlorosilane ($SiHCl_3$). Because of various advantages over these two compounds, including a higher deposition rate, dichlorosilane (SiH_2Cl_2) is now being used, though still to a lesser degree (131). Little health effects information on the chlorosilanes is available. Since they readily react upon contact with small amounts of moisture to form HCl, much of the available information is based on health effects data for HCl (132-134). It has been demonstrated in experimental animals that exposure to 500 ppm of $SiHCl_3$ for 3 minutes causes immediate injury, and exposure to 250 ppm causes delayed injury (personal communication with Dr. C.U. Dernehl, of Union Carbide, Nov. 6, 1979). Trichlorosilane may be especially dangerous upon contact with the eyes, in that signs of exposure may not be evident for 30 to 60 minutes after exposure has ceased (Dr. C.U. Dernehl, Nov. 6, 1979). Unless the Eyes are washed immediately, blindness could result. Exposure may not be immediately evident because of the slower rate of hydrolysis of trichlorosilane. Exposure to 1000 ppm trichlorosilane for 4 hours killed three of six rats, and exposure to 500 ppm for 4 hours killed one of six rats (Dr. C.U. Dernehl, Nov. 6, 1979). Most manufacturers reportedly use a TLV of 5 ppm, based on detection of hydrochloric acid (132-134).

Experimental animals exposed to 700 ppm $SiCl_4$ for 3 minutes suffered immediate severe injury (Dr. C.U. Dernehl, Nov. 6, 1979). An $SiCl_4$ concentration of 4.6 percent in the air killed all rats within 1 hour (53). Much lower concentrations would most likely cause severe disabling injury (DR. C.U. Dernehl, Nov. 6, 1979).

No studies concerning the health effects of dichlorosilanes were found. It is believed that SiH_2Cl_2 is at least as hazardous as $SiHCl_3$ and possibly more so, since it is much more volatile. [The Reid vapor pressure for SiH_2Cl_2 is 276 kPa (40 psia), whereas for $SiHCl_3$ it is only 126 kPa (18.3 psia) (134).]

All three of the chlorosilanes discussed above are extremely corrosive to all human tissues and can cause severe burns. One acute effect from vapor inhalation may be irritation in the upper respiratory tract. Low-level, long-term exposure may lead to chronic effects, such as irritation of the skin and of the upper respiratory tract (135).

Silane, which is produced and used in the Union Carbide alternative process, is not considered as hazardous as its chlorinated counterparts. It is described as being a moderate irritant to the skin, eyes, and mucous membranes. Because it may ignite spontaneously in air, precautions should be taken to prevent contact with air. A TLV of 7 mg/m^3 (0.5 ppm) and an STEL of 2 mg/m^3 have been established for silane (136).

In production of silicon cells, some of the HCl used to produce the chlorosilanes will be unreacted and present in the product gas stream. Most of this is vented to the atmosphere, but some may be present in the workplace. Acute effects of HCl may be irritation of the mucous membranes, eyes, and upper respiratory tract, and pulmonary edema. It is also believed that long-term exposure to low levels may cause hyperchlorhydria (abnormal amount of HCl in the stomach) and promote tooth decay (42). A TLV of 7 mg/m^3 (5 ppm) in air has been adopted for HCl (117).

In one of the alternative processes for production of low-cost SeG-Si, silicon carbide (SiC) is reacted with chlorine gas (Cl_2) to form $SiCl_4$, which is then distilled and reduced with sodium in a hydrogen-argon environment (12). Chlorine reacts with body moisture to form acids, and therefore is very irritating to the skin, eyes, and mucous membranes (124,137). If inhaled in high concentrations it is an asphyxiant, resulting in choking, nausea, vomiting, and syncope (137). Its effects are well known. Other reported effects from chronic exposure include alveocapillary injury, increased airway resistance, decreased vital capacity, hypoxemia, lung function changes, and in animals chronic bronchitis and pneumonitis (137,42). An 8 hour TWA of 1 ppm is the current OSHA standard (123). NIOSH has recommended a 1.45 mg/m^3 (0.5 ppm) ceiling concentration for a 15 minute exposure (123).

Care must be taken to avoid contact with sodium. Metallic sodium is highly reactive with moisture, and upon contact with the skin reacts exothermically with body or tissue moisture causing thermal and chemical burns (110).

In another process being developed for production of SeG-Si, SiF_2 and SiF_4 are used. The SiF_2 at one stage is also developed into a polymeric form (13). Release of these compounds into the air may result in hydrolysis and in formation of hydrated silica, H_2SiF_6, and possibly HF (138). In the process being developed by SRI, a number of fluorinated compounds are used as starting materials, are intermediates in the process, or are byproducts. These include H_2SiF_6, NaF, HF, Na_2SiF_6, and SiF_4. This process, which also uses sodium to reduce SiF_4 to silicon is discussed in more detail in Section 3.1.

Hydrofluoric acid is one of the most corrosive inorganic acids. Upon contact with skin, the fluoride ion penetrates the skin and travels to the deep tissue layers, causing liquifaction neurosis of the soft tissues and decalcification and corrosion of the bone (139). The burns cause intense pain, but the onset of pain after exposure to HF solutions at up to 60 percent strength may be several hours after initial exposure (139). This delayed reaction makes the acid even more dangerous. Exposure to HF has also resulted in various respiratory disorders, such as hemorrhages in the respiratory tract, pulmonary edema, acute pneumonitis, and inflammation of the bronchial tree. Exposure has also resulted in hemorrhaging of the heart and kidneys, and hyperemia in various organs. Chronic exposure to excess concentrations has been found to result in slight skeletal sclerosis. A TLV of 2 mg/m^3 (3 ppm) has been adopted for HF by OSHA. NIOSH has recommended an exposure limit of 2.5 mg F/m^3 (6 ppm) (123). Epidemiologic studies of HF are adequately described in literature (139).

No information concerning human health effects from SiF_4 exposure was found in the literature. The gas is considered highly toxic, and upon hydrolysis it forms hydrated silica, H_2SiF_6, and possibly HF (138).

As with HF, H_2SiF_6 can be expected to be extremely corrosive to the skin, the conjunctiva, and the mucous membranes. Symptoms and illnesses resulting from exposure may be similar to those for HF and fluorides (42). Contact of H_2SiF_6 with the skin, or inhalation or ingestion may result in death or permanent injury after chronic or acute exposures (124). When heated or allowed to contact water or steam, this substance may decompose to emit highly toxic and corrosive fluoride fumes. The LD_{LO} (lowest lethal dose recorded in the literature) for a guinea pig by oral administration is 200 mg/kg and by subcutaneous administration, 250 mg/kg (110).

The acute toxicity to animals of NaF administered by oral, intraperitoneal, subcutaneous, intravenous, and dermal routes is reportedly high (110). Doses of 25 to 50 mg can cause severe vomiting, diarrhea, and central nervous system manifestations (110). The lethal dose to man is taken as 75 to 150 mg/kg (110).

The acute toxicity of Na_2SiF_6 to animals is reportedly high when administered by oral routes and moderate by subcutaneous routes (110). The LD_{50} (dose killing 50 percent of test animals) for a rat by oral routes is 125 mg/kg, and the LD_{LO} for a frog by subcutaneous injection is 448 mg/kg (110).

Additional study is needed to determine the chronic health effects, if any, of these fluorinated compounds, especially if the processes proposed by SRI and Motorola find widespread use.

Two of the processes use sodium as a reductant. Hazards of sodium are discussed above.

In the Battelle process discussed earlier, zinc is reacted with $SiCl_4$ to produce silicon. The potential health effects of zinc are discussed in Section 8.2.3. Zinc chloride ($ZnCl_2$) is given off in the process and recycled into zinc and chlorine. If it escapes into the work area, $ZnCl_2$ may cause mucous membrane irritation.

8.1.3 Preparation of Single-Crystal Silicon Wafers

After the polycrystalline silicon has been produced, it is remelted and subjected to one of the single-crystal growth processes. In the Czochralksi (Cz) process, currently the major commercial method, cylindrical ingots of single-crystal silicon are grown. The ingot then may be bonded to a ceramic submount with hot-melt adhesive or wax and sliced into wafers with a diamond saw or with steel bands to which an abrasive slurry is fed. Prior to the wafer slicing, however, the ingot ends are cut off. The ingot is ground so that it is cylindrical. During these grinding operations silicon dust may be entrained in the air unless ventilation is adequate. During this procedure workers may be exposed to a number of materials. Airborne particulates may be introduced into the work environment from the silicon ingot and from the abrasive slurry used in the multiple-band saw (composed of SiC and mineral-oil-base slurry vehicle). Silicon carbide (carborundum) is considered fairly innocuous, although little information is available. In two reported cases the chest X-rays of workers exposed to carborundum showed modular shadows (42). It was suggested that the harmful effect from carborundum was caused by the liberation of fibrogenic silicon from carborundum by tissue fluids (44). Carborundum is, however, classified as a nuisance dust (TLV, ACGIH = 10 mg/m^3) (OSHA = 15 mg/m^3) (117). The specific organic composition of the mineral-oil-base slurry vehicle was not established, but it is listed as a nonhazardous material for shipping (8).

The mineral oils have relatively low toxicity. Exposure in this application would most likely be from inhalation of mist or fumes. Studies in which animals were exposed to mineral oil mists have shown no significant effects (137). Inhalation of heat-decomposed oil fumes may cause lung irritation (137). A chronic localized tissue response known as lipoid pneumonia has been reported in persons taking mineral-oil-based nose drops over a period of years (42). An exposure limit of 5 mg/m^3 for the mist has been suggested (117).

8.1.4 Surface Cleaning and Etching

In silicon cell production, the sliced wafers are usually etched with a 30 percent NaOH solution, followed by a 1 percent NaOH solution to remove the parts of the wafer damaged by the slicing (8,84). In one process the initial NaOH etch was followed by a rinse in an acid solution of acetic acid, HF, and HNO_3 (13).

Sodium hydroxide (NaOH) is very corrosive to all body tissues, and especially the eyes. Most reported exposures have been by dermal contact. Corrosive action on skin may cause burns and deep ulcerations. There may be a latent period of several minutes after exposure before any irritation is noticed (140).

Severe exposure of the eyes may result in secondary glaucoma, cataracts, or even blindness (140). Inhalation of NaOH may cause irritation of mucous membranes. Ingestion of NaOH has caused severe corrosion of internal organs and narrowing of esophagus and stomach passages. Epidemiological studies are reported elsewhere (140). An 8 hour TWA of 2.0 mg/m^3 in air has been adopted by OSHA (117). NIOSH has recommended a 2 mg/m^3 ceiling limit for a 15 minute exposure (123).

The toxicity of HF is discussed above and the toxicology of acetic acid and HNO_3 is discussed in previous preceeded section.

It is reported that in one plant after the silicon is sliced it is cleaned in solvent baths (27). This cleaning removes organic residues. Some of the solvents reported as being used are methanol; 1,1,1-trichloroethane; detergent; and an acetone/trichloroethylene mixture. Workers in this cleaning area could be exposed to hazardous levels of the solvent vapors if the materials are used in sufficient quantities in an uncontrolled manner.

Overexposure to trichloroethylene (TLV = 100 ppm) can result in headaches, dizziness, vertigo, tremors, nausea, vomiting, fatigue, and drunkenness; unconsciousness and possibly death may occur (141). Trichloroethylene has been found to be a depressant of the trigeminal nerve and possibly a depressant of all nervous tissue (141). Fatalities from acute exposure have been a result of hepatorenal failure following ingestion and ventricular fibrillation (irregular muscle contractions of the heart) following inhalation. Chronic exposure has resulted in disorders of the central nervous system, diplopia, loss of motion, disorders of the cardiovascular system, liver abnormalities, and blindness (141). Addiction of workers to trichloroethylene has also been reported (141). Trichloroethylene has been reported to cause liver cancer in mice but not in rats (123).

Acetone is considered a relatively safe solvent with a TLV of 1000 ppm (117) except that it is highly flammable. Skin irritation from dermal exposure and headaches from inhalation have been recorded (124).

Methanol possesses distinct narcotic properties. It is also a slight irritant to the mucous membranes, with a TLV of 262 mg/m^3 (200 ppm) for inhalation (117). Its main effect is exerted upon the nervous system, particularly the optic nerves and the retina (42,124,125,137). The effect upon the eyes has been attributed to optic neuritis, which subsides but is followed by atrophy of the optic nerve (124). Once absorbed, methanol is eliminated only very slowly (42, 124,125,137). Coma resulting from massive exposure may last as long as 2 to 4 days. In the body the products formed by its oxidation are formaldehyde and formic acid, both of which are toxic. Because of the slowness with which it is eliminated, methyl alcohol should be regarded as a cumulative poison. Though single exposures to fumes may cause no harmful effect, daily exposure may lead to accumulation of sufficient methanol in the body to cause illness (124).

Methyl chloroform, or 1,1,1-trichloroethane, is a narcotic (42,124,137) and a skin defatting agent (42). Acute poisoning at high concentrations in air has resulted in death due to respiratory depression (42,117). Symptoms of acute exposure include dizziness, incoordination, drowsiness, unconsciousness, and death (137). Exposure of animals for 3 months at concentrations from 1,000 to 10,000 ppm caused some pathologic changes in the liver and kidneys (117). Methyl chloroform is considered by some to be the least hepatotoxic of the common chlorinated hydrocarbon solvents (excluding methylene chloride) (117). An 8 hour TWA of 1,910 mg/m^3 (350 ppm) has been established for methyl chloroform (117). A ceiling limit of 1910 mg/m^3 (350 ppm) has been recommended by NIOSH (123).

A mixture of hydrogen peroxide (H_2O_2) and sulfuric acid (H_2SO_4) has also been used for cleaning silicon wafers. Hazards associated with both of these chemicals are discussed later.

Another reported method of cleaning and etching is by use of a plasma gas (26,28,31). In one plasma etching process, the use of carbon tetrafluoride (CF_4) and hydrogen fluoride (HF) is reported (28). Toxicology of HF is discussed above. One source indicates that CF_4 appears to be less chronically toxic than carbon tetrachloride (CCl_4) and also that acute toxicity by inhalation is low (124). Because chronic exposure to CCl_4 has been reported to cause cirrhosis, it is suggested that areas where CF_4 is used be well ventilated. Toxicology of fluorinated hydrocarbons is discussed in Section 8.1.2.

The greatest potential hazards are due to skin contact, particularly from soiled gloves or clothing. To prevent allergic reactions to dermititis problems, personal work practices must be monitored, including the use of dry clean gloves which should be changed daily or more frequently if necessary.

A surface texturing etch to reduce light reflection and improve metal adhesion may be performed using NaOH, followed by cleanings with hot trichloroethane and methane (26). Hot potassium hydroxide (KOH) and plasmas have also been used for texture etching (24,26). Except for KOH, the hazards associated with these chemicals are discussed above. The effects of KOH are very similar to those of NaOH. It is very corrosive to body tissues, and dermatitis may result from repeated exposure to dilute solutions (137). Systemic effects are due entirely to local tissue injury (137). Extreme pulmonary irritation may result from inhalation of dust or mist (137).

8.1.5 Junction Formation (Doping)

Boron Dopants--

After the wafers are sliced, etched, and cleaned, they are electrically characterized by the addition of dopants. Dopants commonly used in silicon cell production are boron (p-type), and phosphorous (n-type). Boron trichloride (BCl_3) gas is most often used for deposition of boron in the silicon. The BCl_3 dissociates at the silicon surface to allow the free boron to diffuse into the silicon (6). Boron trichloride may be emitted into the work environment during doping and during purification of the silicon. The toxic action of the halogenated borons is influenced by their decomposition products (137). As with the chlorosilanes, BCl_3 hydrolyzes upon contact with moisture to emit HCl fumes (143). The LC_{LO} level for BCl_3 by inhalation over a 7-hour period is 20 ppm in rats and mice (144). Animal experiments with halogenated borons have shown a fall in inorganic phosphorous level in blood and on autopsy, pneumonia and degenerative changes in renal tubules (137). Chronic exposure leads to irritation of the respiratory tract, dysproteinuria, reduction in cholinesterase activity, and increased nervous system lability (137). Besides HCl, boric acid is another decomposition product of BCl_3 (143). Boric acid may be absorbed through the skin, especially in burned or cut areas. It is reported that application of boric acid to burns or cuts has caused death in humans (124,137). The most notable symptoms include depression of the central nervous system and gastrointestinal irritation (124,125). Chronic effects of boron toxicity have been reported as being anorexia, mild gastrointestinal irritation, loss of appetite, nausea, and erythymatous rash (137).

Phosphorous Dopants--

The phosphorous dopant may be applied to the wafer by converting phosphine (PH_3) or phosphorous oxychloride ($POCl_3$) to phosphorous pentoxide (P_2O_5). When PH_3 is used the following reactions take place:

$$2\ PH_3 \xrightarrow{713^\circ} K + 3H_2 + 2P$$

Oxygen is then provided to produce phosphorous pentoxide:

$$4P + 5O_2 \rightarrow 2P_2O_5$$

$$2P_2O_5 + 5\ Si \rightarrow 4P + 5\ SiO_2$$

Phosphorous oxychloride ($POCl_3$) is obtained as a liquid. Oxygen or an oxygen-nitrogen mixture is then bubbled through the liquid $POCL_3$, and the gas is passed through a diffusion tube furnace. As with the use of phosphine, a glass layer containing phosphorous is grown on the silicon wafer. Potential emissions from the tube furnace exit are H_2, HCl, P_2O_5, PH_3, and Cl_2 (125,145). The P_2O_5 forms a glassy layer upon contact with the silicon wafer. This process takes place in a tube furnace and is referred to as chemical vapor deposition (CVD). Workers may be exposed to PH_3, $POCl_2$, or P_2O_5 while loading the furnace. At the furnace exit, P_2O_5, $POCl_3$, and H_3PO_4 may be present. Some of these could possibly enter the work environment should the exhaust system be faulty or inadequate.

Symptoms from acute phosphine inhalation may be fatigue, nausea, vomiting, gastric pain, diarrhea, headache, thirst, oppression in the chest, and burning substernal pain (124,137). Coma or convulsions may precede death. Exposure to low levels of phosphine may result in chronic poisoning, characterized by anemia, bronchitis, gastrointestinal disturbances, and disturbance of visual, speech, and motor functions (124). The lowest published lethal dose by inhalation for humans is 8 ppm. The adopted TLV value is 0.4 mg/m^3 (0.3 ppm) (117).

Phosphorous pentoxide (P_2O_5) is a highly caustic and very corrosive material. It may react vigorously with moisture, evolving heat (124). No health effects information on P_2O_5 was found. Phosphorous oxychloride ($POCl_3$) is reported to be an intense irritant that may evolve toxic chloride and PO_x fumes on contact with moisture or on thermal decomposition (124). It is also believed to act in a fashion similar to chlorine gas (42). The toxicology of chlorine gas is discussed above.

Studies on the acute effects of $POCl_3$ on rabbits gave the following results (146):

OLD_{50} (oral lethal dose required to kill 50 percent of animals) - 36 mg/kg

DLD_{50} (dermal lethal dose required to kill 50 percent of animals) - >631, <1000 mg/kg

Inhalation of vapors at a concentration of 159 mg/liter for 18 minutes killed six of six rabbits exposed. The material is considered highly toxic by ingestion and moderately toxic by dermal applications. It is also corrosive to the skin and eye tissues. Phosphorous hexafluoride (PF_6) and pentaethyl phosphate are two other phosphorous-containing dopants that may be used more in the future (33). The latter is used as a spin-on dopant (33). No toxicity information was found in the published literature on these substances. Before they are accepted for widespread use, more health effects data is needed.

Hazards associated with HCl and Cl_2 are discussed above. Hydrogen (H_2) is another possible emission from the tube furnace. Though hydrogen is an asphyxiant, the levels that produce this effect probably will not be reached in this application. The most prominent danger with hydrogen is explosion. Care must be taken in construction of exhaust systems to ensure the safe removal of hydrogen gas.

Doped Wafer Etching--

Following the phosphorous doping, the outer surface of the wafer consists of an SiO_2 layer and a phosphorous layer. To remove this SiO_2 layer and expose the p-layer, an acid etch is performed with hydrofluoric (HF) and nitric (HNO_3) acids. The toxicology of HF acid is discussed above.

Nitric acid is extremely corrosive to tissues. Upon contact with HNO_3, the skin turns a yellow to brown color. Contact with the eyes causes immediate opacification of the cornea and conjunctive epithelia, which may be permanent and cause blindness (117).

Acute exposure to HNO_3 by inhalation is characterized by dryness of the nose and throat, cough, dyspnea, and upper respiratory irritation. Bronchial pneumonia, pulmonary fibrosis, and cyanosis have also resulted from acute exposures (147).

Long-term exposure to HNO_3 may result in chronic bronchitis, chemical pneumonitis, and dental erosion (147). A TLV of 5 mg/m^3 (2 ppm) has been adopted (123). Several epidemiological studies are discussed elsewhere (147).

Etching of the wafer may release SiF_4 gas (8). No information concerning human health effects from SiF_4 exposure was found in the literature. The gas is considered highly toxic, and upon hydrolysis it forms hydrated silica, H_2SiF_6, and possibly HF (138). Toxicology of H_2SiF_6 and HF is discussed in Section 8.1.2.

Ion Implantation--

An alternative method of junction formation being investigated is ion implantation. In this technique pulsed electron beams are used to implant the dopant (phosphorous, arsenic, and boron are presently being used) in the desired concentration and depth (31).

The toxicology of arsenic is discussed later with respect to production of gallium arsenide photovoltaic cells. One arsenic-containing dopant that is used for junction formation is arsenic hexafluoride (AsF_6) (133). No toxicity data was found in the published literature on this substance.

No toxic effects have been noted for elemental boron (137). Toxicology of boron trichloride (BCl_3) and halogenated borons in general is discussed above.

Worker illness has been reported associated with the hydrides of boron, called boranes. Of the three boranes--diborane, decaborane, and pentaborane--pentaborane is the most hazardous. Because of its volatility, diborane has caused respiratory tract symptoms. Repeated exposures to diborane are reported to lead to complaints of headache, dizziness, chills, muscular weakness, and tremors. Experimental chronic exposures (7 to 10) at concentrations from 1.1 to 6.8 mg/m^3 (1.1 to 6.8 ppm) killed some animals (125). Autopsy revealed rhinitis (inflammation of nasal mucous membranes), pneumonia, and some structural lung damage (125). The TLV set by the ACGIH for diborane is 0.1 mg/m^3 (0.1 ppm). Drowsiness, nausea, headache, and vertigo have followed decaborane exposures. The LD_{50} for a 4-hour exposure to decaborane is reported to be 120 to 230 mg/m^3 (20 to 38 ppm) (125). The ACGIH has established a TLV of 0.3 mg/m^3 (0.05 ppm) for decaborane. In man, chronic exposures to pentaborane may result in nausea and drowsiness (125). The ACGIH has established a TLV of 0.01 mg/m^3 (0.005 ppm) for pentaborane. Upon exposure at higher levels, muscle pain and spasms, tremors, and convulsions occurred and persisted for 48 hours. Abnormalities of hepatic and renal function were reported (42). Decaborane and pentaborane are also poisons to the central nervous system (125).

Other boron-containing dopants that may see more frequent use include boron trifluoride (BF_3) and triethyl borate $B(OC_2H_5)_3$ which is used as a spin-on dopant (33).

Boron trifluoride is a severe pulmonary irritant leading to pneumonia in animals upon repeated exposure (42). Exposure to levels of 100 ppm resulted in a uniformly high mortality rate in six laboratory species and 15 ppm was occasionally fatal in 30-day studies. On the basis of these preliminary studies, a tentative limit of 1 ppm was set. Moreover, it had been assumed that BF_3 hydrolyzes rapidly and almost completely in air to HF and the relatively nontoxic boric acid. Since 1 ppm of BF_3 releases 3 ppm (the threshold limit value) of HF, the 1 ppm value seems an appropriate standard for BF_3 (117).

Recent toxicologic studies of BF_3 show that BF_3 does not hydrolyze so rapidly or completely as had been presumed, but is toxic *per se* (117). Rats, rabbits, and guinea pigs were exposed five days a week for months to boron trifluoride at concentrations of 12.8, 3-4 and 1.5 ppm. Chronic toxicity involved pneumonitis and dental fluorosis. At the lowest value, there was only marginal evidence of pneumonitis. Thus, while the original basis for the treshold limit value of 1 ppm appears to be in some question, the value nevertheless appears adequate, though possibly with little margin of safety. Torkelson et al. have suggested a limit of 0.3 ppm or below to prevent pulmonary irritation. A ceiling value of 1 ppm, if faithfully applied, should be adequate to prevent lung injury (117).

Little toxicological information is available on triethyl borate. Its toxicity is virtually unknown, and more information is needed on potential health effects from this compound.

The form of phosphorous used in ion implantation was not reported. Toxicology of some phosphorous compounds is discussed above. Acute effects from inhalation of phosphorous vapors in industry are rare (117). Some animal experiments indicate that acute systemic poisoning may follow skin burns (137). Upon contact with the skin, phosphorous may cause severe burns that are necrotic, yellowish, and fluorescent under ultraviolet light (137). If the victim survives acute poisoning, a symptomatic latency period from a few hours to a few days may follow, usually resulting in death from dysfunction or failure of the liver, kidney, or cardiac or vascular systems (137).

In cases of chronic exposure phosphorous acts on the periosteum and the subperiosteal bone (42). Secondary clinical signs in humans include polymorphic leucopenia, susceptibility to bone fracture, and the inability of alveolar bone to resorb following extractions (137). A TLV of 0.1 mg/m^3 has been established for phosphorous (117).

Another method of junction formation being investigated is with polymer dopants. This procedure is also by diffusion except that dopants in liquid or paste form are applied by spinning on, rolling on, or screening (31). Spin-on dopants may consist of an organic silicate, an alcohol, and a small proportion of the desired dopant in organic form. Again, the dopants being used are phosphorous, arsenic, and boron. Some spin-on dopants include tetraethyl orthosilicate, triethyl borate, and pentaethyl phosphate (155). No toxicological information was found in the published literature on these substances, and studies are needed to determine potential acute and chronic health effects before they are widely used. Other polymer dopants reported contain P_2O_5 and P_2O_3 (personal communication with Don Bickler, et al., JPL, Feb. 5, 1979).

Hazards associated with P_2O_5 are discussed above, and the hazards associated with P_2O_3 are similar. Phosphorous trichloride may cause severe burns if it comes in contact with the eyes, skin, mucous membranes, or gastrointestinal tract (148). Flash fires may also occur upon contact with moisture. Moreover, P_2O_3 may also decompose to PH_3 upon exposure to moisture or heat (124). Toxicology of PH_3 is also discussed above.

After they are etched, the wafers may again be solvent-cleaned by use of xylene, methanol, or trichloroethylene. Health effects of methanol and trichloroethylene are discussed in a previous section. Xylene also has narcotic effects on the central nervous system, and variable effects on the liver and kidneys (149). Chronic exposure may affect the heart and vascular system (117).

For worker exposure to xylene, NIOSH has set a limit of 434 mg/m^3 (100 ppm), time-weighted average, for a 10-hour workday, 40-hour workweek. A ceiling concentration of 868 mg/m^3 (200 ppm) has been recommended by NIOSH (123).

It should be noted that not all of the single-crystal ingot formed is suitable for slicing wafers. The unusable portion of the ingot is treated with HF and HNO_3 acids to remove the oxide layer on the surface and is then remelted. Exposure to HF, HNO_3, and SiF_4 is a potential hazard in this process (8).

8.1.6 Metallization

Metallization involves vacuum deposition, plating, or printing of a metal contact that provides for current collection.

Metals used in vacuum deposition processes include silver and sequential layers of titanium-palladium-silver. The toxicology of titanium and palladium is discussed in Sections 8.1.7 and 8.3.3 respectively.

Absorption of silver compounds in the body results in deposition in various tissues, which leads to a disorder known as argyria, in which the skin pigmentation becomes grayish. This condition usually develops over a long period of exposure (2 to 25 years). Once deposited in the tissues, silver cannot be eliminated and tends to accumulate (43,124,125,137). One study has also shown that subcutaneous and intravenous injection of colloidal silver produced tumors in experimental animals (68).

Plating metallization is usually done with nickel, sometimes preceded by gold layer to increase the contact reliability. The toxicology of these metals is discussed in Sections 8.2.2 and 8.3.3 respectively. In the plating method the metallization pattern is usually defined by a silk screen or photoresist. One silk screen pattern was developed using a petroleum wax dissolved in isopropyl alcohol, and then dried. Further information on photoresist compositions is needed to assess their toxicity. Potential hazards of isopropyl alcohol are discussed in Section 8.3.3. One screen-printed contact contained silver, aluminum, silica, and an organic binder. Exact compositions are unknown, as this was considered proprietary information (8). Some of these contacts may be copper-based also. The toxicology of these substances is discussed elsewhere.

If screen-printed contacts are applied, the organic binder is driven off by heating the wafer (8). The composition of the organic binder should be determined to allow evaluation of its potential health effects.

8.1.7 Antireflective Coating

Following the contact application, an antireflective coating is applied. The coating commonly consists of silicon nitride (Si_3N_4), titanium dioxide (TiO_2), a combination of TiO_2 and SiO_2 (8,17), SiO (25), or TaO_2 (17,52). The coating may be spun on or vacuum deposited (8,16,17). Although no information was found on TiO_2, titanium compounds in general are considered physically inert. The TiO_2 dust, however, is placed in the nuisance category, and an exposure limit of 10 mg/m^3 is recommended (117).

No systemic industrial poisoning from tantalum compounds has been reported, although some are suspected to cause skin irritation and mild fibrosis of the lungs. Information specific to tantalum dioxide was not found. The TLV for tantalum is 5 mg/m^3 (117).

No toxicological information was found in the published literature on Si_3N_4. Since this material is being used increasingly, more information is needed on its potential hazards.

Potential health effects from SiO_2 exposure are discussed above. No data are available to indicate whether any of the SiO_2 used in antireflective coatings is in free crystalline form. Although levels of these antireflective coatings in the workplace are probably low, they should be determined and adequate precautions taken to prevent continued exposure.

8.1.8 Module Assembly

After the individual cells are completed, they may be tested individually or placed into modules for testing. In one instance a xenon lamp was used to simulate sunlight (27). During the testing it is possible that ozone and oxides of nitrogen might be found in the workplace.

Because of their relatively low solubility in water, the nitrogen oxides (primarily NO_2) are only slightly irritating to the mucous membranes of the upper respiratory tract (124,137). Their warning power is therefore low, and the workman may inhale dangerous amounts of the fumes before noticing any real discomfort. Relatively high concentrations (60 to 150 ppm) cause immediate irritation of the nose and throat, with coughing and burning in the throat and chest. These symptoms often clear up on breathing fresh air, and the workman may feel well for several hours. Some 6 to 24 hours after exposure, he develops a sensation of tightness and burning in the chest, shortness of breath, sleeplessness, and restlessness. Dyspnea and air hunger may increase rapidly, with development of cyanosis and loss of consciousness, followed by death. When an exposed person recovers from the pulmonary edema, there is usually no permanent disability but pneumonia may develop later. Concentrations of 100 to 150 ppm are dangerous for short exposures of 30 to 60 minutes. Concentrations of 200 to 700 ppm may be fatal after even very short exposures (124).

Continued exposure to low concentrations of the fumes, insufficient to cause pulmonary edema, is said to result in chronic irritation of the respiratory tract, with cough, headache, loss of appetite, dyspepsia, corrosion of the teeth, and gradual loss of strength (124).

Because exposure to nitrous fumes is always potentially serious, persons so exposed should be kept under close observation for at least 48 hours (124).

The potential for high levels of NO_x exposure from xenon lamps used in quality control testing of photovoltaic arrays would appear minimal, though no data on exposure were found in the literature.

A TLV of 30 mg/m^3 (25 ppm) in the workplace has been established for NO, and 9 mg/m^3 (5 ppm) for NO_2 (123). NIOSH has recommended a ceiling exposure limit of 1.8 mg/m^3 (1 ppm) for a 15 minute exposure to NO_2 (123).

Ozone, if inhaled in sufficient concentrations, may cause death from pulmonary edema (125). Irritation of mucous membranes of the eyes, nose, and throat may occur in poorly ventilated areas where X-ray machines or ultraviolet lamps are used (42). Long-term low-level exposures to ozone may possibly cause chronic obstructive pulmonary disease in man (42). A TLV of 0.2 mg/m^3 (0.1 ppm) in the workplace environment has been established, although a level of 0.05 ppm has been suggested for prolonged inhalation (42).

Interconnection--

In module assembly the wafers are placed on a backing substrate and conductively connected by soldering or welding individual cells and wires where needed. This grouping of wafers constitutes a module. The back supports commonly used are aluminum, Plexiglas^R, glass, acrylics, or epoxy fiberglass board. Handling of fiberglass board may cause skin irritation. Inhalation of fibrous glass particles may cause coughing, nosebleed, and sore throat. Inhalation has caused rupture of small arteries in the upper respiratory tract, requiring surgery to correct the condition (42). Use of epoxy resins with fiberglass may enhance its irritant effect, especially to skin. It is also suspected that fiberglass of a certain particulate size may cause fibrosis in the lungs (124). The evidence that inhalation of fibrous glass results in pulmonary disease is not well established. The ACGIH has determined that no known serious health risk is associated with exposure to fibrous glass (117).

The term "epoxy resins" covers a wide range of materials, and the specific composition of those that may be used with the fiberglass board in solar cell backing was not determined. Following are a few generalizations concerning the health hazards of epoxy resins. An epoxy resin has two basic components: the resin and a curing agent. The curing agent presents the primary health hazard, as it is usually a type of amine. Secondary amines may cause dermatitis, erythema, severe burns, and sometimes sensitization (42, 124,127). Inhalation of fumes can cause irritation of the mucous membranes and asthma-like reactions (42,127). Direct contact of amines with the eyes may cause severe damage (127). Amine hardeners may cause bronchospasm and coughing episodes that last for several days after exposure ends (42). Organic anhydrides and polyamides may also be used as curing agents. Organic anhydrides may cause irritation of the eyes, nose, and throat (42,127). Industrial problems resulting from use of hardeners are fairly common.

A typical epoxy resin is prepared with epichlorohydrin and a polyhydroxy compound (e.g., bisphenol A) in the presence of the curing agent (42). As with the amine curing agents, epichlorohydrin and bisphenol A are also skin irritants and sensitizers (42).

Bisphenol A, or diglycidyl ether (DGE), may cause severe irritation of the eyes, respiratory tract, and skin (127). It may cause ecchymosis followed by coagulation necrosis upon skin contact (117,127). DGE is a suspect carcinogen.

Diglydicidyl ether is regarded as a hazardous compound, and skin contact should be avoided. A TLV of 0.5 ppm has been established for DGE (117).

One epoxy resin hardener, 4,4'diaminodiphenylmethane (DDM), an aromatic amine, has been shown to have carcinogenic potential in experimental animals (150).

The above discussion of epoxy resins concerns uncured resins. A completely cured epoxy resin is very stable, has high resistance to heat and chemicals, and has little or no toxic effects. There is some evidence, however, that when cured resins are sawed, drilled, machined, or otherwise subjected to procedures that generate high degrees of local heat, degradation products may form that could be harmful (153). Some believe these may contain free amines (153). Toxicity of fumes and gases of cured epoxy thermal decomposition products has also been studied (154). The LC_{50} for rats for a 1-hour exposure to decomposition products is estimated to be 3.2×10^5 mg min/m^3. Autopsy showed that the main cause of death was respiratory failure resulting from pulmonary edema. Histotoxic anoxia and organic alterations to renal or hemopoietic systems may have contributed to the death (155).

Two other substrate materials being used are polyvinyl butyrate and ethyl vinyl acetone (3). Finished vinyl plastics have been found to be without injurious properties (42). Limited animal experiments with the monomer vinyl butyrate suggested low toxicity (124). The information available is not sufficient to allow any conclusions, however. No information was found concerning the toxicology of ethyl vinyl acetone. Both of these materials should be evaluated further in relation to potential health effects.

Methyl ethyl ketone is sometimes used to clean contacts in the module before the brazing solder is applied. Though methyl ethyl ketone may be slightly irritating to the eyes and upper respiratory tract, there is no evidence of industrial organotoxicity (42). The TLV of methyl ethyl ketone is 590 mg/m^3 (200 ppm) (117).

The brazing solder is usually a lead/tin or silver/lead/tin alloy. The primary concern in the soldering operation is exposure to lead. The soldering operation causes the release of lead suboxides and other fumes into the air (42,156). Upon inhalation, the lead compounds are absorbed in the respiratory tract and accumulate in the body to a point where symptoms associated with lead poisoning begin to occur (124).

Compliance with the OSHA lead standard of 0.05 mg/m^3 should provide adequate worker protection.

The acid fluxes used for soldering, usually zinc chloride (156, 158), ammonium chloride (156), hydrochloric acid (74), or stannous chloride, may also irritate the mucous membranes of the eyes, throat, nose, and lungs. In some brazing and soldering operations, fluxes or resin co-solders may release formaldehyde and/or fluoride fumes (156,158).

Formaldehyde also causes irritation of the skin, respiratory tract, and eyes and has teratogenic effects in rats (159). Frequent exposure may result in hypersensitivity (9,124,159). Acute irritation of the respiratory tract has resulted in pulmonary edema, pneumonitis, and death (159). OSHA standards for formaldehyde are an 8 hour TWA of 3 ppm; an acceptable ceiling of

5 ppm and a maximum ceiling of 10 ppm (30 minutes) (123). NIOSH has proposed a ceiling limit of 1.2 mg/m^3 (1 ppm) for a 30 minute exposure (123).

Chronic exposure to fluorides may result in anemia, weight loss, bone and dental defects, and eosinophilia, and in young workers may impair growth (124). Welders exposed to fluoride fumes complained of respiratory and eye irritation, nausea, and nosebleeds (117).

Encapsulation--

In the module assembly procedure the entire array is next encapsulated with a transparent protective coating, which may be glass, silicone rubber, silicon-based resin, or similar material. Some potential cover materials being looked at are soda-lime glass, low-expansion-coefficient borosilicate glass, acrylic, FEP Teflon, Saran, Tedlar, and Mylar (7). Potential sealants are acrylic, polyvinyl butyral, and polysulfides (7). Potential adhesives are acrylic, epoxy, FEP Teflon, and methyl phenyl types of RTV silicones (7). Toxicology and health hazards for most of these materials have not yet been characterized. Health hazards of epoxy materials are discussed above. It is important that these facts be considered when these materials are evaluated for future use.

At one plant a silicon-based resin was used as the encapsulating material. Preparation of the resin involved the use of 2-propanol and methyl ethyl ketone among other chemicals, which were not specified (35). These two solvents have relatively low toxicity ratings, but the identity of the other chemicals should be established.

This study found no mention of wire coatings used in solar cell construction. In the electronics industry, however, polyurethanes are widely used as a protective coating for wires, because they can be easily soldered through (158,160). The heating of polyurethanes releases dangerous cyanide and diisocyanate vapors (160). At workroom levels of 10 ppm in air, the body can usually convert cyanide to the relatively nontoxic thiocyanate (42). The toxicology of potassium cyanide is a representative of most alkali cyanides and HCN in their action.

An 8 hour TWA of 5 mgCN/m^3 (10 ppm) has been adopted for dermal exposure to alkali cyanides, and hydrogen cyanide (123). It has been shown that concentrations of diisocyanate and/or cyanide in the immediate vicinity of soldering operations can exceed threshold limit values (160).

Summary--

Because module assembly will be one of the most labor-intensive operations involved in solar cell production, there exists the potential for a more recently discovered disorder to occur. It is known as industrial mass psychogenic illness, and is believed to be caused by a combination of physical and psychological job stresses and other life stresses (161-164). It usually develops suddenly and spreads rapidly in a well-defined population (i.e., workplace, school) in the absence of an identifiable toxic agent. Most reported cases occur in female workers engaged in boring and repetitive jobs in an atmosphere of poor labor-management relations. The primary symptoms include headaches, dizziness, lightheadedness, weakness, sleepiness, nausea, bad taste in mouth, and blurred vision.

Although physical stress brought on by noise, air contamination, poor lighting, temperature variations, truck and forklift exhaust fumes, or odor from solvents and glues may be the stimulus that initiates the psychogenic reaction, it is not the cause of the illness.

Most operations in present or future solar cell manufacturing facilities are or will be automated; some activities, however, particularly module assembly and possibly interconnect operations, will be labor-intensive. These operations contain the ingredients necessary to invoke a psychogenic response in workers. Suggestions to prevent the occurrence of psychogenic illness include:

1. Maintenance of good management-labor relations.
2. Allowing some social interaction between employees during working hours.
3. Reducing the potential for boredom.
4. Providing adequate work space for each individual.
5. Instituting preplacement screening to let the prospective worker see where he (she) will be working, and thus providing workers ill suited for this type of work an opportunity to reject before starting work.
6. Including in the preplacement medical examination questions to identify people with asthma, allergy predisposition, or those not psychologically suited to work in such closed-in areas.
7. Providing visual access to the outdoors.

8.2 POTENTIAL HAZARDS IN PRODUCTION OF CADMIUM SULFIDE CELLS

Two processes, the back-surface cell-spray process and the front-surface cell-vacuum process, have been proposed or used for commercial production of cadmium sulfide/copper sulfide (CdS/Cu_xS) solar cells (8). The primary health concern in the manufacture of CdS/Cu_xS cells will be exposure to cadmium and cadmium compounds.

In addition to Cu_xS, materials being investigated for use as absorbers in the CdS cell include cadmium tellurium (CdTe), indium phosphate (InP), copper indium selenide ($CuInSe_2$), and copper indium sulfide ($CuInS_2$). Because some of these materials may be used commercially in the future, the potential hazards of their use are discussed briefly.

8.2.1 Exposure to Cadmium and Cadmium Compounds

Exposure of workers to cadmium may occur in various operations directly or indirectly associated with the manufacture of CdS solar cells. Such operations include zinc mining and smelting, refinement of cadmium from baghouse dusts, production of CdS, handling of CdS powder, and deposition of CdS on the solar cell substrate.

The two primary methods by which CdS is deposited on the cell substrate are vacuum deposition and spraying, though sputtering is widely used also. Fugitive dust from vacuum deposition and sputtering will probably be minimal (84). The spray technique presents a greater probability of worker exposure to cadmium. Because these processes are still in the developmental stages, a total assessment of the potential occupational and health hazards must await the implementation of full-scale operations and the results of emission monitoring.

When cadmium is ingested, 6 to 10 percent of the quantity ingested is absorbed. It is carried in the red blood cells and concentrates primarily in the kidneys. Ingestion causes nausea, vomiting, diarrhea, and gastrointestinal pain and discomfort. Oral ingestion usually is not fatal because vomiting often occurs immediately after ingestion so that little of the cadmium is absorbed (42,124,125).

Inhalation of cadmium fumes and dusts may cause coughing, headaches, dyspnea, tightness in the chest, and vomiting. The first stage of acute inhalation exposure may result in pulmonary edema, and even death by anoxia. In fatal cases, fatty degeneration of the liver and inflammatory changes in the kidneys have been noted. The second stage results in cellular prolification in the alveoli, hyperplasia of the living cells, and occasional intraalveolar hemorrhage. This may be followed by pulmonary fibrosis and emphysema (125). It has been shown that freshly generated cadmium fumes are more acutely poisonous than "old" settled fumes (42).

Chronic exposure by inhalation of cadmium oxide fumes, dusts, sulfides, and stearates may result in anorexia, anemia, emphysema, proteinuria, bone fracture, rickets, loss of smell, and hypertension (42,124,125,137). Another result of cadmium exposure may be yellowing of the tooth enamel (42,124,125,137), which is an indication that a worker is being overexposed.

It has been demonstrated that chronic cadmium poisoning is progressive and that illness may progress even after the worker's exposure has been terminated. Moreover, cadmium is a suspected carcinogen. NIOSH conducted a retrospective, epidemiological investigation of workers exposed to cadmium at a primary cadmium smelter (165). The investigation was undertaken because of the conclusiveness of the carcinogenic effects of cadmium by injection in experimental animals and because of the spectrum of nonmalignant and malignant respiratory, renal, prostatic, and other chronic effects reportedly or conclusively produced by occupational exposures to cadmium and its compounds. The results of the NIOSH study show significantly increased mortality due to total malignancies, lung cancer, and prostatic cancer among cadmium smelter workers. The results also confirm the findings of earlier occupational studies and strongly implicate cadmium exposure as a cause of certain types of malignant disease. Parenteral injection of rodents with cadmium powder and with cadmium in the sulfide, oxide, sulfate, and chloride forms induced sarcomas at the sites of injection (145,166). Of 14 rats given a 50 mg intramuscular dose of CdS, 5 developed tumors 9 to 15 months after injection (166). Established OSHA standards for cadmium are as follows: 0.1 mg/m^3 for an 8 hour TWA (fume); 0.3 mg/m^3 ceiling limit (fume); 0.2 mg/m^3 for 8 hour TWA (dust); 0.6 mg/m^3 ceiling (dust) (123). NIOSH recommended standards are 40 μg Cd/m^3 TWA, and 200 μg Cd/m^3 ceiling (15 minute exposure) (123).

8.2.2 Production of Back-Surface Cells

A process currently being developed by Plant K, uses window glass as a cover on which a CdS layer is sprayed and a Cu_xS layer is deposited by ion exchange. It is reported that the Cu_xS layer was originally sprayed on in a combination of copper acetate and N,N,-dimethylthiourea plus other chemicals (8). Before application of these layers a tin oxide layer is applied by spraying a solution of tin chloride ($SnCl_4$) and methanol on the hot (400°-500°C) glass substrate. Various metal contacts, collectors, and electrodes are deposited by vacuum evaporation. According to one source an Inconel contact, a copper electrode, a copper collector, and a lead coating between the Cu_xS and copper electrode were evaporated on the cell (8).

Because some inorganic tin salts, especially the halogenated ones, are irritants and can liberate toxic fumes on decomposition, emissions from this process should be controlled to protect workers. When $SnCl_4$ in methanol is applied to a hot surface, it is likely that acid fumes are liberated.

When tin salts gain access to the blood stream, they are highly toxic, producing paralysis and other neurologic damage (117). Tin hydride (SnH_4) has been shown to be more toxic than arsine to mice and guinea pigs. A TLV in air of approximately 0.2 mg/m^3 has been adopted for arsine (117), but no value for SnH_4 has yet been adopted. Because the exact nature of the tin salt and other chemicals used is not known, it is difficult to assess the total potential hazards to workers. The dusts and fumes of tin and tin oxides have caused in industrial workers a benign pneumoconiosis known as stannosis (42,117,125,137). Tin oxides are currently classified as nuisance particulates, with a TLV of 10 mg/m^3 (124).

Since the $SnCl_4$ is mixed with methanol, organic tin compounds may be formed and given off upon contact with the hot substrate. There are numerous organic tin compounds, whose toxic reactions and effects vary widely. Many organic tin compounds, especially the alkyltin compounds, are highly toxic when ingested. A chlorinated organic tin, tributyl tin chloride, showed a much greater hemolytic effect than the dibutyl or tetrabutyl compounds (137). This indicates that the chlorinated organic tin compounds may be yet more toxic than nonchlorinated organic tin compounds. Though many organic tin compounds have yet to be investigated, an 8 hour TWA of 0.1 mg/m^3 has been established by OSHA to prevent systemic toxicity (123).

In the deposition of the CdS layer, $CdCl_2$ and thiourea are used. Various other compounds that might also be used include the following (47):

Cd	S
Cadmium propionate	N,N,-dimethylthiourea
Cadmium acetate	Allyl thiourea
Cadmium formate	Thiolacetic acid
Cadmium nitrate	2-thiozoline-2-thiol
	ammonium thiocynate

Toxicity of cadmium compounds is discussed above. When given to rats, $CdCl_2$ caused severe anemia (42). Recent studies showed that inhalation of 3 to 300 ppm $CdCl_2$ increased mortality rates in mice, over those of a control group, by 7 to 26 percent. Apparently the $CdCl_2$ rendered the mice more susceptible to infectious agents, since deaths were attributed to the protozoan flagellate hexamita (84).

Thiourea has caused bone marrow depression resulting in anemia, leukopenia, and thrombocytopenia in animals (110). It has also caused liver, thyroid, and epidermoid sarcomas in experimental animals (167). Extensive feeding periods were needed to produce the tumors. Even though the ability of thiourea to induce tumors appears to be low, worker exposure to the chemical should be controlled. Upon heating, thiourea emits toxic films of SO_x (124). Toxicological information on the other sulfur compounds is scarce. No information could be found in the literature on N,N,-dimethylthiourea, thiolacetic acid, or 2-thiozoline-2-thiol.

No toxicological information specific to ammonium thiocyanate, which is used as a herbicide, was found in the literature. It is recorded that thiocyanate salts have produced goiters in animals (42). Although the thiocyanates do not normally disassociate into cyanide, heating or contact with acids may lead to emission of cyanide fumes (124). Thiocyanates normally have low acute toxicity, but prolonged exposure may produce skin rashes, running nose, nausea and vomiting, dizziness, or mild or severe nervous system disorders (124). Allyl thiourea has been reported to cause contact eczema in humans through sensitization to the compounds (124). An LD_{50} of 200 mg/kg is reported for oral ingestion in rats (144).

Both processes being developed for commercial cell production use copper baths, in which the cells are dipped to form the Cu_xS layer. Another method that has been described is spray deposition of copper acetate, N,N,-dimethyl thiourea, and other proprietary compounds (8).

Although no information was found in the published literature concerning N,N,-dimethyl thiourea, it is considered a potential hazard on the basis of the toxicity of thiourea.

Copper compounds in general are considered fairly safe. Inhalation of copper dust by experimental animals has caused hemolysis of the red blood cells, deposition of hemofuscin in the liver and pancreas, and injury to the lung cells (124). Injection of the dust has caused cirrhosis of the liver and pancreas, and a condition closely resembling hemochromatosis, or bronzed diabetes (124). Considerable exposure of human beings to copper compounds has not resulted in such diseases. Inhalation of copper dusts, fumes, and mists of copper salts (such as copper acetate) may cause congestion of the nasal septum (137). Fumes and dusts have also been known to cause metal fume fever, which is characterized by chills, dryness in the throat, coughing, oppression in the chest, and nausea (42). Salts reaching the gastrointestinal tract may cause nausea and vomiting, gastric pain, hemorrhagic gastritis, and diarrhea (137).

Persons afflicted with Wilson's disease, a chronic condition, show an abnormally high absorption, retention, and storage of copper in the body (124,137).

A TLV of 0.2 mg/m^3 has been adopted for copper fumes, dusts, and mists (117).

After application of the CdS and Cu_xS layers in back-surface cell production, a chemical resist is applied. This may be by photomechanical screen printing, whereby a photoresist is printed on the surface and subsequently developed, or, as described above, by application with a needle. The resist protects the underlying materials against etching, deposition, or detrimental effects of other processes that follow. Solvents used in the formulation of resists are the primary health concern. N-butyl acetate, used in photoresists is associated with allergic response and sensitization. One resist material was composed of modified vinyl resins in methyl ethyl ketone (168). In general, solvents may cause drying and cracking of skin, sensitization, and increased susceptibility to infection. Prolonged exposure may result in chronic liver and kidney damage or in effects on the central nervous system and cardiovascular system. In one incident solvent vapors from drying resists eventually built up to concentrations that caused the operator acute discomfort (160). No information on vinyl resins was found in the literature.

After the resist is applied, the cell may be etched to remove the unwanted portions of the CdS and Cu_xS layers. In the process used by Plant K, temporary strips of resist are applied, and then are peeled off after application of appropriate coatings. A broad range of etchants may be used. Those used in the electronics industry are HCl, HF, H_3PO_4, HNO_3, $FeCl_3$, ammoniacal chlorite, ammonium persulfate [$(HN_4)_2S_2O_8$], and chrome/sulfuric acid solutions (158,160,169). In fabrication of solar cells, potassium cyanide (KCN) has been used in at least one instance (63). Health effects of HCl and HF are discussed in Section 8.1.2; those of HNO_3 are discussed in Section 8.1.5.

Inhalation of fumes from phosphoric acid (H_3PO_4) may cause irritation of pulmonary tissues and possibly acute pulmonary edema (137). Chronic exposure to these fumes may lead to cough, bronchitis, and pneumonia (137). The TLV for H_3PO_4 (1 mg/m^3) is based on experience and on toxicological data for sulfuric acid (117). This acid is considered less dangerous than either nitric or sulfuric acids (117).

Ferric chloride is a relatively safe etchant. It is a dermal irritant, and the aerosol is irritating to the respiratory tract (137). The only other immediate danger is that HCl fumes may be emitted if ferric chloride is decomposed by heat or reaction with water (124).

Little information was found in the literature on the toxicology of ammonium persulfate. Its acute and chronic local toxicity is reportedly low, however (124). From an industrial hygiene standpoint, the only danger of this compound is that it is a powerful oxidant and could cause an explosion if it comes into contact with a reducing agent.

The main health concern with the chrome/sulfuric acid solution is the presence of chromium. Toxicology of sulfuric acid is discussed in Section 8.3.3. A major problem with exposure to chromium is dermatitis. Dermal sensitization may also occur (42, 137). Ulceration or perforation of the nasal septum and other exposed areas is a common occurrence among workers exposed to chromium dusts or mists (42,124,125). Acute exposure to chromium dusts or mists may cause coughing, headache, dyspnea, anorexia, and fever (137). It is reported that chromate workers suffer a high incidence of bronchitis (42). Although rare, disturbances of the hepatic system (125,137) and central nervous system (125) have been reported. Epidemiological studies show that chromate is most likely a lung carcinogen (42,124,125,137,145) and has also led to cancers of the nose, pharnyx, and sinus (124,145). Recent evidence shows that hexavalent and not trivalent chromium compounds were mutagenic in certain strains of E. coli (145).

Potassium cyanide (KCN), like most cyanides, is a fast-acting poison that inhibits a respiratory enzyme responsible for oxidation of tissues. This often results in death by asphyxiation. One industrial death from inhalation of potassium cyanide fumes has been reported (42). Chronic exposure to alkaline cyanide solutions may cause a condition known as cyanide rash, which is characterized by itching areas and papular and vesicular eruptions (42,124). Cases have been reported where exposure to KCN or solutions containing KCN resulted in weakness, abdominal pain, vomiting, headache, severe vertigo, signs of meningitis, cetaxia, pruritis, and tachycardia (42). Another case involved a gold plater who had worked at the profession for 20 years, 10 of which were in a shop with insufficient ventilation (42). Case histories are discussed elsewhere (42).

After the etching is completed, the cell is washed. According to one source an Inconel^{R} contact is applied by vacuum evaporation (8). This is in the back-surface cell process. Inconel is a nickel-based alloy containing approximately 16 percent chromium and 7 percent iron. Although the vacuum evaporation is an enclosed process, the fumes could enter the workplace environment by way of faulty pump seals or other faulty or damaged equipment, or during loading and unloading operations. Chronic exposure to respirable particles of nickel can cause cancer (42, 117, 124,125,137,145). The areas usually affected are the lungs and nasal passages. The most common symptom of exposure to nickel and nickel compounds is referred to as "nickel itch" (42, 117,124,125,137,145). This is a form of dermatitis characterized by itching and burning papular erythma, usually on the hands and arms. This type of dermatitis resembles atopic or neurodermatitis rather than eczematous contact dermatitis (137,145). An 8 hour TWA of 1 mg/m^3 has been established for inorganic nickel dust and fumes by OSHA (123). NIOSH has recommended a TWA of 15 ug Mi/m^3 (123).

Following the application of the Inconel^R contact, another resist application may be made. According to one source, this is followed by vacuum evaporation of a positive electrode lead coating, and subsequently a copper electrode (8). Toxicological information on lead and copper is discussed above. Plant K did not report the metals used for contacts, electrodes, and other components, since these are considered proprietary.

The final operation is a heat treatment. The heat treatment area should be suitably ventilated because high temperatures could cause volatilization of screen or photoresists or other chemicals used in the process that were not completely removed prior to this step. Volatilization could result in generation of solvent or other chemical fumes in the area.

8.2.3 Production Of Front-Surface Cells

In one proposed process, a zinc coating is applied to a copper foil substrate followed by deposition of a CdS layer, a Cu_2S layer, and an SiO_2 cover (8). Plant L, however, uses a steel substrate. The back coating is not known. Because all of these applications take place within a vacuum chamber, significant exposure of workers to the chemicals is restricted except when the chamber is cleaned or materials are handled prior to deposition. Unless the vacuum system is isolated, leaks from pumps and piping, constitute a potential route into the work environment. The toxicity of SiO_2 is discussed in Section 8.1.1. Hazards associated with cadmium and copper are discussed in Sections 8.2.1 and 8.2.2 respectively.

The zinc compound used in the process is not known. Zinc compounds in general are considered relatively innocuous. Zinc oxide dust can cause "brass chills," or metal fume fever (124,125, 137) and also may cause a papular, pustular eczema by clogging the subaceous gland ducts (124,137). Zinc chloride fumes can cause lung damage and death if inhaled in high enough concentrations. Exposure to zinc chloride fumes may also cause damage to the mucous membranes of the nose, throat, and respiratory tract, resulting in a pale gray cyanosis. Dermal exposure to zinc chloride has resulted in ulceration (42,124,125,137). Workers in zinc refining operations have suffered from nonspecific intestinal, respiratory, and nervous conditions (124). There is no evidence that industrial zinc poisoning is associated with increased incidence of cancers of any type (145).

SES reportedly uses copper, nickel, and gold layers for contact grids. Toxicity of copper and nickel is discussed in Section 8.2.2. Toxicity of gold is discussed in Section 8.3.5.

Before deposition of any of the layers, the copper foil substrate goes through a degreasing step. Plant L has used Freon as the degreaser. The electronics industry has used chloroform, xylene, Freons, methylene chloride, toluene, ethyl acetate, cellosolve, trichloroethylene, and trichloroethane (158,160). The TLV's of these substances are presented below, followed by a brief review of their toxicity. Xylene, trichloroethylene, and trichloroethane are discussed in Section 8.1.4.

	TLV (117)	
Degreasing solvent	ppm	mg/m^3
Chloroform	10	50
xylene-skin	100	435
most Freons	1000	
methylene chloride	100	360
toluene-skin	100	375
ethyl acetate	400	1400
cellosolve (ethyleneglycol)	100	250
trichloroethylene	100	535
1,1,1 trichloroethane	350	1900

Fluorochlorohydrocarbons, or Freons have relatively low toxicity. The Freons or decomposition products may produce mild irritation of the upper respiratory tract and occasionally dermatitis (124, 137). Exposure to high concentrations may result in mild depression of the central nervous system (42,137). Dizziness has been reported after inhalation exposure to 5 percent dichlorofluoromethane, and unconsciousness after exposure to 15 percent dichlorofluoromethane (137). The primary hazards from exposure to high concentrations of Freons are narcosis, anesthesia, and asphyxia (42,124). Cardiotoxic effects, such as irregular heartbeat, thought to result from sensitization of the heart to epinephrine, may be caused by exposure to certain Freons (42). Cardiac arrythmias, with sudden death, have occurred from breathing some of these chemicals (137). Table 8-1 lists Federal standards for selected fluorocarbons of economic importance.

TABLE 8-1. FEDERAL STANDARDS FOR SELECTED FLUOROCARBONS OF ECONOMIC IMPORTANCE

Compound	Federal standards	
	ppm	mg/m^3
Bromotrifluoromethane fluorocarbon 13B1	1000	6100
Dibromodifluoromethane fluorocarbon 12B2	100	860
Dichlorodifluoromethane fluorocarbon 12	1000	4950
Dichloromonofluoromethane fluorocarbon 21	1000	4200
Dichlorotetrafluoroethane fluorocarbon 114	1000	7000
Fluorotrichloromethane fluorocarbon 11	1000	5600
1,1,1,2-tetrachloro-2,2-difluoroethane fluorocarbon 112	500	4170
1,1,2,2-tetrachloro-1,2-difluoroethane fluorocarbon 112	500	4170
1,1,2-trichloro-1,2,2-trifluoroethane fluorocarbon 113	1000	7600

(From Ref. 137).

Cellosolve (monoethyl ether of ethylene glycol) is not considered a highly toxic solvent, but acute poisoning may produce effects on the central nervous system and kidneys. Symptoms resulting from action on the central nervous system may be headache, drowsiness, weakness, slurred speech, stuttering, tremor, and blurred vision. Renal effects from acute poisoning can lead to albuminuria and hematuria. Cellosolve is also an irritant to the skin and mucous membranes. Chronic exposure may possibly result in anemia (42).

Ethyl acetate, because of its ability to dissolve fats will cause cracking and drying of the skin upon contact (42,124,125). The vapors are also irritating to the mucous membranes and eyes, and repeated or prolonged exposures may cause conjunctival irritation and corneal clouding (42, 124,125). High concentrations have a narcotic effect and may cause congestion of liver and kidneys (124).

Chronic exposure to ethyl acetate may result in secondary anemia, leucocytosis, nervous symptoms, and fatty degeneration of the viscera (42,124).

Methylene chloride has a powerful narcotic action and was once used as an anesthetic; it is still used for local anesthesia in Europe (170). It also causes irritation of the eyes and respiratory tract. Several effects on the central nervous system and behavioral effects have been reported. Women exposed during labor were said to have experienced retrograde amnesia. Epileptiform attacks have been reported in both humans and animals after being anesthesized with methylene chloride (170). One worker exposed over a period of 3 years complained of forgetfullness, insomnia, a feeling of drunkenness, and auditory and visual hallucinations. Other workers experienced increased fatigue, headaches, and nervous disorders after exposure for 1.5 to 2 years (702). Laboratory animals exposed to methylene chloride have shown changes in liver and kidney function (170).

The current TLV for methylene chloride is 500 ppm. Because exposure to 500 to 1000 ppm has caused depression of the central nervous system in some persons, a new TLV of 100 ppm is to be adopted (123,170). NIOSH recommends a 261 mg/m^3 (75 ppm) TWA (123).

Acute poisoning from inhalation of toluene may lead to irritation of the conjunctiva and upper respiratory tract, impairment of coordination and reaction time, severe fatigue, extreme nausea, insomnia, headache, skin paresthesias, anorexia, intoxication, and coma. Because toluene dissolves fats readily, prolonged contact with skin results in drying, cracking, and dermatitis. Splashing of toluene in the eyes has caused corneal damage (171).

Cases of addiction to toluene have been reported (171). Chronic poisoning has resulted in electroencephalographic abnormalities and even in permanent encephalopathy (171).

Epidemiological studies on workers exposed to toluene at concentrations of approximately 200 ppm have shown no pathological changes in bone marrow and no significant effects on the rate of chromosome changes in peripheral blood lymphocytes (713). An 8 hour TWA of 200 ppm, with an acceptable ceiling limit of 300 ppm and a maximum ceiling limit of 500 ppm (10 minute) has been established by OSHA (123). NIOSH has recommended a TWA of 375 mg/m^3 (100 ppm) and a 750 mg/m^3 (200 ppm) ceiling limit (123).

Chloroform, once a widely used anesthetic, has been abandoned for this use because of its toxic effects (124,137). Acute poisoning by inhalation results in pupil dilation, irritation of mucous membranes and skin, inebriation, anesthesia, and narcosis (124,125, 137). Acute poisoning has also resulted in depression of the central nervous system, kidney damage, liver necrosis, heart damage, and even death due to respiratory arrest or liver damage (124,125,137). Chronic overexposure may also result in enlargement of the liver and kidney damage (137). Oral administration has caused hepatomas in mice (124)).

The ACGIH currently lists chloroform as an industrial substance suspect of carcinogenic potential for man. They have set a TLV of 120 mg/m^3 (25 ppm) (117,124,137). NIOSH has recommended a ceiling limit of 9.78 mg/m^3 (2 ppm) for a 60 minute exposure (123).

In production of the front-surface cell described by Gaudel et al. (8), copper was used as the substrate. Other substrates used have been molybdenum, silver, and conductive glass and plastics (46). A zinc or other coating is applied to metal substrates to prevent the CdS from forming a rectifying contact with them, and also is applied to the glass or plastic substrate to ensure an ohmic contact (46). SES uses a steel substrate, but the nature of the back contact is proprietary.

No toxic effects of molybdenum in industry have been reported (42,137). Molybdenum trioxide may cause irritation of the eyes and mucous membranes of the nose and throat (137). Inhalation by animals of molybdenum trioxide dust at high concentrations has caused anorexia, diarrhea, loss of muscular coordination, and high mortality rate (137). Large oral doses of ammonium molybdenum have produced some fetal deformities in rabbits (137).

Deposition of zinc or other back-contact material is followed by vacuum deposition of the CdS layer. The Cu_xS layer that follows may be deposited by an ion exchange technique using copper or cuprous chloride as the starting material (51). Other methods for depositing the Cu_xS layer are reactive sputtering (51), vacuum evaporation (50), and sulfurization of copper in a h-hydrogen sulfide/hydrogen atmosphere. Acute exposure to H_2S (15 minutes or longer at concentrations of several hundred ppm) may result in respiratory difficulty, pulmonary edema with hemorrhage, respiratory depression, neural damage (central or peripheral), and abnormalities of the cardiovascular system (72). Subsequent effects of acute exposure may be epilepsy, acoustic-nerve neuritis, abnormal ECG, and amnesia. Contact of H_2S with the eyes may cause a painful conjuntivitis, possibly with corneal erosion, photophobia, and lacrimation (137,172). Exposure to H_2S in concentrations over 1000 ppm usually results in death.

Little evidence of effects from chronic exposure has been cited in the literature. A number of studies have indicated that subacute effects, particularly brain damage, may occur. There are also reports that low-level, long-term (hours) exposures to H_2S may cause conjunctivitis and that residual effects such as abnormal ECG and brain damage may be caused by brief massive exposures (172). An acceptable ceiling of 200 ppm and a maximum ceiling of 50 ppm (10 minutes) has been adopted by OSHA (123). NIOSH has recommended a ceiling limit of 15 mg/m^3 (10 ppm) for a 10 minute exposure (123).

8.2.4 Other Materials Used In Cadmium Cell Production

In an effort to increase cell efficiencies, various absorber materials other than Cu_2S are being investigated. The primary materials include cadmium telluride (CdTe), copper indium selenide ($CuInSe_2$), copper indium sulfide ($CuInS_2$), and indium phosphide (InP) (7,52,77). Others being investigated are silver indium selenide ($AgInSe_2$), copper gallium sulfide ($CuGaS_2$), copper gallium telluride ($CuGaTe_2$), and variations of Cu_xAg_{1-x} $InSe_2S_{2(1-y)}$ and $CuAl_yGa_{(1-y)}Se_{z(1-z)}Te_{2z}$. Health effects information on these specific materials was not found in the published literature. Health effects associated with exposure to cadmium, copper, silver, gallium, and tellurium are discussed in other sections of this report.

There are no reported cases of human illness from indium exposure, but occupational exposure has not yet been studied (42). Patch testing of workers showed neither irritant properties nor evidence of sensitization (42). Oral administration of indium to animals has proved to be nontoxic. Intraperitoneal, subcutaneous, and intravenous injection however, has caused hindleg paralysis liver and kidney damage, muscle degeneration, convulsions, and death in experimental animals (42,125).

Elemental selenium has low acute systemic toxicity, but dust or fumes can cause serious irritation of the respiratory tract (124, 137). Acute irritation of the eyes, nose, and throat has been reported in workers briefly exposed to high concentrations of selenium fume (117). Acute selenium poisoning may produce central nervous system effects, which include nervousness, drowsiness, and sometimes convulsions (125). Inorganic selenium compounds can cause dermatitis (42,124,125,137). Garlic odor of breath is a common symptom (42,124,125,137,145). Industrial exposure to hydrogen selenide produces "garlic" breath, nausea, dizziness, and lassitude. Eye and nasal irritation may occur. In experimental animals 10 ppm is fatal (125). Selenium ocychloride, a vesicant, presents an industrial hazard. In rabbits, 0.01 ml applied dermally resulted in death (125).

It has also been suggested that selenium causes fetal toxicity and teratogenic effects in humans (125,145). Chronic toxicity studies with experimental rodents has shown that the liver is the primary target organ, subject to atrophy, necrosis, cirrhosis, and hemorrhage (145). Other affected organs are the kidneys, heart, pancreas, and spleen.

Symptoms of chronic inhalation exposure to selenium include pallor, coated tongue, gastrointestinal disorders, nervousness, "garlic" breath, liver and spleen damage, anemia, mucosal irritation, and lumbar pain. It has been suggested that some of these symptoms are due to tellurium impurities since tellurium is present in selenium ores (125). Selenium is a suspected teratogen and carcinogen of the liver and thyroid, though these effects have not been seen in man (124,137,145). One study showed that workers exposed to selenium suffered from skin rashes, indigestion, irritability, and fatigue (42). There have also been reports of an increase in dental cavities in persons living where the soil has a high selenium content (42). A TLV of 0.2 mg/m^3 has been adopted for selenium compounds (117).

8.3 POTENTIAL HAZARDS IN PRODUCTION OF GALLIUM ARSENIDE CELLS

Production of GaAs cells first involves the purification of gallium and arsenic. The high-purity gallium and arsenic are next subjected to reaction within an evacuated quartz bottle by heating each individually and allowing the vapors to react. The resultant polycrystalline GaAs is melted in a single-crystal growing chamber, along with a dopant (usually silicon, tin, tellurium, or germanium), and a solid single-crystal ribbon ingot or boule (n-type) is pulled from the molten GaAs. After the crystal is grown, it is cleaned and sliced. An additional n-type GaAs layer (usually doped with tin, tellurium, or silicon) is epitaxially deposited on the wafers in a vacuum, followed by deposition of a p-type GaA/As layer, doped with germanium, zinc, magnesium, or beryllium.

Following is a discussion of the possible occupational and health hazards associated with materials that are used or have potential for use in the production of GaAs photovoltaic cells. It must be recognized that production of these cells is currently limited to laboratory-scale operations. If single-crystal GaAs cells are used in photovoltaic solar systems, sunlight concentrator systems will be used in conjunction with them. Hazards associated with concentrator systems are discussed under installations, Section 7.

8.3.1 Production and Purification of Gallium

Relatively few potential health hazards appear to be associated with production and purification of gallium. One incident of industrial illness due to exposure to gallium fluoride fumes has been reported (42). Symptoms resulting from exposure were skin rash, and pain and weakness in the muscles supplied by the radial nerve. In animals gallium acts as a neuromuscular poison, causing renal damage and damage to the intestinal tract (42,125). Photophobia, blindness, and paralysis in rats have been reported (125). In dogs aplastic changes in the bone marrow have been observed (125).

The hazards associated with NaOH, which is used in gallium extraction, are discussed in Section 8.1.4

8.3.2 Production and Purification of Arsenic

Probably the greatest occupational hazard associated with production of GaAs photovoltaic cells is the potential exposure to arsenic. The nature and severity of arsenic toxicity is highly dependent on the chemical form and oxidation state of the arsenic involved. It is generally true that trivalent arsenic compounds are more toxic than pentavalent compounds. Poisoning from arsenic compounds may be acute or chronic. Acute poisoning usually results from swallowing arsenic compounds; chronic poisoning results from either swallowing or inhalation (124).

Acute arsenic poisoning (from ingestion) leads to marked irritation of the stomach and intestines, with nausea, vomiting, and diarrhea. In severe cases the vomitus and stools are bloody, and the patient goes into collapse and shock, with weak, rapid pulse, cold sweats, and coma; death may occur (124,137).

NIOSH has recommended a ceiling limit of 2 μg As/m^3 for a 15 minute exposure (123). The federal standard is 10 $\mu g/m^3$ on a time weighted average (179).

8.3.3 Cell Fabrication

Single Crystal Production--

In fabrication of photovoltaic cells, the polycrystalline GaAs, formed as described above, is then melted down, electrically characterized with a dopant, and placed in a growing chamber, where a single crystal is pulled. A liquid blanket of boron oxide is maintained over the GaAs to control loss of vaporized As in Plants M and N surveyed. The dopant, usually tin (72), germanium (8,77), or tellurium (7,72), is most likely added by vapor diffusion. Health effects associated with tin and silicon are described elsewhere.

It has been reported that worker exposure to tellurium may result in a garlic odor of the breath, scaly and itchy skin, anorexia, nausea, vomiting, and somnolence (124). No serious cases of industrial tellurium poisoning have been reported; however, the accidental injection of tellurium into three persons suffering from retrograde pyelography resulted in the death of two (125). Symptoms observed were stupor, cyanosis, vomiting, garlic breath, and loss of consciousness (125). Tellurium hydride (H_2Te) has been found to be a powerful hemolytic poison in experimental animals (42). Exposure to H_2Te also may produce symptoms such as headache, malaise, weakness, dizziness, and respiratory and cardiac symptoms in humans (137). If the tellurium is added to GaAs in the same manner as palladium, workers could potentially be exposed to H_2Te. A TLV of 0.1 mg/m^3 has been established for tellurium (117).

Boron oxide aerosols are reported to have very low toxicity (117). Exposure of rats and dogs to boron oxide dusts at relatively high concentrations (rats, 470 mg/m^3 for 10 weeks; dogs, 57 mg/m^3 for 23 weeks) caused no deaths or other signs of intoxication other than mild nasal irritation in rats (117). In view of the low toxicity, a TLV of 10 mg/m^3 has been adopted (117).

The toxicity of germanium and its compounds is low except for the hydride (GeH_4), which is a toxic hemolytic gas. Acute effects on animals from germanium oxide (GeO) exposure are hypothermia, listlessness, diarrhea, respiratory and cardiac depression, edema, and hemorrhage in the lungs and respiratory tract (125). Germanium tetrachloride ($GeCl_4$) and tetrafluoride (GeF_4) are irritants of the skin and mucous membrane, and germanium dioxide (GeO_2) is an eye irritant (42,137). Germanium tetrachloride is also an upper respiratory tract irritant and may cause bronchitis or pneumonitis (137). Prolonged exposure to high concentrations may damage the liver, kidney, and other organs (137).

Chronic administration of GeO at 1000 ppm in food or 100 ppm in water to rats caused growth inhibition and mortality (125). A TLV of 0.6 mg/m^3 has been adopted for GeH_4 (124).

Wafer Preparation--

After the polycrystalline GaAs has been melted, and a single crystal pulled, it is sliced with reciprocating multiple band saws or diamond saws. This cutting will most likely release fines and dust of the GaAs material, some of which may become airborne and possibly inhaled by workers. In its undissociated state GaAs has been found to be fairly nontoxic when administered to rats orally. The LD_{50} reported was 4700 mg/kg (176). More toxicological information is needed on GaAs dusts and fumes to allow assessment of the potential hazards.

After the crystal is sliced, the wafers are cleaned with sulfuric acid and hydrogen peroxide. As mentioned above, Plant M also uses several solvents including acetone, trichloroethylene, methanol, and isopropyl alcohol. Health effects of all these solvents except isopropyl alcohol are discussed earlier.

Isopropyl alcohol may be mildly irritating to the conjunctiva and mucous membranes in the upper respiratory tract (55). There have been no reported cases of industrial poisoning from exposure to isopropyl alcohol, though it may be narcotic in high concentrations (137). An 8 hour TWA of 400 ppm has been established for isopropyl alcohol (117).

Dermal exposure to concentrated sulfuric acid (H_2SO_4) will result in immediate burns and possibly even charring of the skin. This causes great pain and if much of the skin is involved, the exposure is accompanied by shock, collapse, and symptoms similar to those seen in victims of severe burns. Action on the mucous membranes and eyes is even more rapid. Splashing of H_2SO_4 in the eyes can cause permanent corneal damage and possibly blindness. Dilute H_2SO_4 will not char the skin, but does irritate the skin and mucous membranes and can cause dermatitis. Exposure to H_2SO_4 mists may result in irritation of the mucous membranes, eyes, and respiratory tract epithelium, and corrosive effects on the teeth. Inhalation of concentrated vapor or mists from hot sulfuric acid or oleum can cause rapid loss of consciousness with serious damage to lung tissue. A single overexposure to H_2SO_4 may lead to acute laryngeal, tracheobronchial, and pulmonary edema (177). Repeated or prolonged inhalation of H_2SO_4 mist can lead to chronic bronchitis. Epidemiological studies have shown that, in comparison with unexposed workers, workers who were exposed to H_2SO_4 showed higher incidence of respiratory disease (especially bronchitis) and dental erosion, and in one study a reduction in vital capacity (28).

Little health effects information was found on hydrogen peroxide (H_2O_2). Because it is a powerful oxidizing agent, it can cause severe skin irritation, depending on the strength of the solution. Blisters are likely to occur upon exposure to solutions of 35 percent H_2O_2 or greater. The eyes in particular are sensitive (124,137). Another hazard involving concentrated H_2O_2 is that it may explode when subjected to heat or mechanical shock or upon decomposition (124).

Epitaxial Growth Processes--

After cleaning of the wafer an additional n-GaAs layer, doped with silicon, tin, or tellurium, is deposited. This is done in vacuum using a liquid-phase epitaxial (LPE) growth process. The toxicology of these materials is discussed earlier.

Again, the GaAs must be melted at temperatures at which a significant arsenic vapor pressure may occur, with potential for leakage of arsenic into the work environment. The manner in which the silicon, tin, or tellurium dopants are added to the GaAs was not described in the literature, though it is probably by vapor diffusion.

Following the LPE-deposited n-GaAs layer, a p-GaAs layer is deposited by LPE. This layer may be doped with beryllium, magnesium, germanium, or zinc. Health effects of germanium and zinc are discussed above.

Inhalation of magnesium may cause conjunctivitis, nasal catarrh, and coughing up of discolored sputum (125). Inhalation of freshly generated magnesium oxide may cause metal fume fever (125,137). Exposure of wounds, scratches, or cuts to metallic magnesium may result in chemical gas gangrene (42), which is characterized by severe inflammation of the exposed area with accompanying blebs. These lesions heal slowly. Although high incidence of digestive disorders has been attributed to magnesium absorption, the evidence is scant (137).

Beryllium and its compounds are highly toxic. Skin lesions are the most common sign of beryllium exposure in industry. Three distinct types of skin lesions have been described: dermatitis, ulceration, and granulomas. The dermatitis, sometimes accompanied by acute conjunctivitis and corneal ulceration, has been regarded as a hypersensitizing reaction. The finding that victims of chronic beryllium lung disease react positively to patch tests supports this notion and indicates the possible immunological component of the chronic disease (125). Exposure to soluble beryllium compounds may cause nasopharyngitis, a condition characterized by swollen and edematous mucous membranes, bleeding points, and ulceration. These symptoms are reversible when exposure is terminated (137). Entrance to the body is almost entirely by inhalation. The acute systemic effects of exposure to beryllium primarily involve the respiratory tract and are manifest by a nonproductive cough, substernal pain, moderate shortness of breath, and some weight loss. An intense exposure, although brief, may result in severe chemical pneumonitis with pulmonary edema (137). Edema may become so severe that right-side heart failure occurs (125).

Chronic beryllium disease is an intoxication arising from inhalation of beryllium compounds. The following limits have been adopted by OSHA for beryllium: 2 $\mu g/m^3$ for 8 hour TWA; 5 $\mu g/m^3$ acceptable ceiling; 25 $\mu g/m^3$ maximum ceiling for 30 minutes exposure (123). NIOSH has recommended an exposure limit of 0.5 $\mu g/m^3$ for 130 minutes (123).

Metallization--

After a grid pattern has been etched, the front contacts of Pd, Au-Zn, Pd-Ag, Au-Mg, or Ag-Zn and back contacts of Sn, Au-Sn, or Au-Ge-Ni, are next applied by vapor deposition. Plant M used a hydrogen bromide - bromine solution for etching.

Bromine and hydrogen bromide and its aqueous solutions are extremely irritating to eyes, skin, and mucous membranes of the upper respiratory tract. Severe burns of the eye may result from exposure to liquid or concentrated vapors. Liquid bromine splashed on skin may cause vesicles, blisters, and slow-healing ulcers. Continued exposure to low concentrations may result in acne-like skin lesions. These are more common in the oral use of sodium bromide as a sedative (137).

Other effects from chronic exposure have been reported in Soviet literature; e.g., loss of corneal reflexes, joint pains, vegetative disorders, thyroid dysfunction, and depression of the bone marrow. These effects have not been reported in the U.S. literature (137).

Hydrogen bromide (hydrobromic acid) is less toxic than bromine, but is an irritant to the mucous membranes of the upper respiratory tract. Long-term exposures can cause chronic nasal and bronchial discharge and dyspepsia. Skin contact may cause burns (137). With the exception of gold and palladium, the potential health effects of the individual metals used for contacts were discussed earlier.

Gold intoxication has been associated with its therapeutic use rather than industrial use and imposes only a minor threat to workers. Most toxic reactions described are as a result of injection of gold salts into persons suffering from arthritis or certain rare skin diseases. Dermatitis and stomatitis are the more common reactions reported. Also reported, however, are nephritis with albuminuria, encephalitis, gastrointestinal damage, hepatitis, aplastic anemia, thrombopenia, and agranulocytosis (42,125).

Little health effects information is available on palladium. Oral administration of 1 grain daily to treat tuberculosis has not resulted in toxic effects. Intravenous injection of 0.5 to 1.0 mg/kg in experimental animals has produced damage to the bone marrow, liver, and kidney (124). Where a colloidal form of palladium was injected subcutaneously to control obesity, a significant loss of weight occurred but was accompanied by fever, local necrosis, and a hemolytic effect (42).

Following contact application, a layer of silver or gold may be electroplated to the ohmic contacts to increase conductivity. An antireflective coating of TiO_2, Ta_2O_5/SiO_2, Ta_2O_5, or Si_3N_4 is then deposited, usually by vapor deposition. Potential health hazards associated with tantalum, titanium, and silicon were discussed earlier. No information was found concerning Si_3N_4, but since this material is becoming widely used, more toxicological information is needed.

8.3.4 Fabrication of Thin-Film Gallium-Arsenide Cells

Fabrication of thin-film GaAs solar cells has included a few materials that are not reported as used in single-crystal GaAs construction. In one instance deposition of the GaAs film is accomplished with arsine (AsH_3) and trimethylgallium (TM-Ga) (76,79).

No toxicological information was found in the published literature on TM-Ga or organic gallium compounds. Though metallic gallium has been found to be fairly nontoxic, organic derivatives may be much more dangerous. Toxicological properties of this compound should be further evaluated.

Substrate materials being used in fabrication of thin-film polycrystalline GaAs cells include tungsten/graphite, germanium/ Kovar^R, and molybdenum/Kovar (71,76,80).

Tungsten deposition was accomplished by thermal reduction of tungsten hexafluoride (WF_6) in a hydrogen atmosphere and passage of this gas over the substrate (76,81). No information on health hazards associated specifically with WF_6 was found in the literature. Oral toxicity of a tungsten compound depends on the salt. In animals parenteral administration caused nervous prostration, diarrhea, coma, and death (125). Oral toxicity has not been a problem in man (125). Effects of tungsten inhalation are controversial; it is not yet known whether tungsten or cobalt is the cause of pneumoconiosis found among workers in the tungsten carbide tool industry (125). Any release of fluorine would probably be as HF. Inhalation of elemental fluorine produces effects similar to those caused by HF. Toxic effects of HF are discussed in Section 8.1.2.

Kovar^R, a nickel/iron alloy, is similar to Inconel^R. The toxicology of Inconel is discussed in Section 8.2.2. Toxicology of molybdenum was also discussed earlier.

In the fabrication of thin-film GaAlAs/GaAs solar cells, trimethylaluminum (TM-Al) is substituted for some of the TM-Ga in order to produce the GaAlAs layer. Although no specific information was found concerning the toxicology of TM-Al, it is noted that related alkyl compounds, which are used as catalysts, show strong irritant properties and high toxicity (124). TM-Al is also dangerous in that it reacts violently with air and water. It may explode on contact with moisture (124).

Dopants used in the manufacture of thin-film GaAs cells include zinc, selenium, and antimony. Zinc is applied in the form of diethyl zinc. Toxicology of zinc was discussed earlier. Little information on diethyl zinc or organic zinc compounds was found. One source lists zinc as a toxic material that is spontaneously flammable in air (124).

Health effects of selenium and selenium hydride (the form in which the selenium is applied) are discussed in Section 8.2.4.

Antimony (Sb) is also mentioned as a dopant used in thin-film GaAs fabrication. The form in which it is applied was not noted. Antimony and antimony compounds are proven skin irritants. Lesions usually appear on moist areas of the body but rarely on the face (137). Antimony dusts and fumes are also irritants of the eyes, nose, and throat, and may cause gingivitis, anemia, and ulceration of the nasal septum (137). The toxic effects of antimony are well established.

Symptoms of chronic oral poisoning by antimony are dry throat, nausea, headache, sleeplessness, loss of appetite, and dizziness. Liver and kidney degenerative changes are late manifestations (137). A TLV of 0.5 mg/m^3 for antimony and compounds has been adopted by the ACGIH (117).

Antireflective coatings reported as used in thin-film GaAs cell fabrication are tantalum oxide (Ta_2O_5), niobium oxide (NB_2O_5), and antimony oxide (Sb_2O_3). Health effects of antimony compounds are discussed above. Potential health hazards of tantalum compounds are discussed in Section 8.1.7.

The toxicology of niobium is relatively unknown. Mice given water containing 5 ppm, minimum, plus 1.62 mg/g in the diet showed liver degeneration (125). In vitro studies indicate that niobium may inhibit adenosine triphosphatase (125). Intravenous injection of 30 mg/kg potassium niobate to dogs and rats produced nephrotoxic effects (125). Niobium pentachloride has reportedly produced moderate transient irritation of the eye and severe dermal irritation (125). There are no known reports of niobium toxicity in man (125).

8.4 POTENTIAL HAZARDS IN PRODUCTION OF AMORPHOUS SILICON CELLS

The toxicology of most chemicals used in the fabrication of amorphous silicon cells is discussed in the toxicology sections pertaining to single-crystal silicon, cadmium sulfide, and gallium arsenide cells. The toxicology of zirconium oxide, which is used as an antireflective coating, is discussed below.

Zirconium compounds have a low order of toxicity (42,117,125,127). Although granulomas in humans and animals have resulted from application of deodorant containing an organic zirconium compound (42,117,125,137), short-term studies exposing five different animal species to zirconium oxide dust at 75 and 11 mg Zr/m^3 showed no adverse effects (117). Two 1-year studies of inhalation exposure to the oxide dust also showed no deleterious effects (117). This zirconium oxide does not appear to present a health hazard. A TLV of 5 mg/m^3, and an STEL of 10 mg/m^3 have been recommended for zirconium compounds (136).

REFERENCES

1. Costello, D., et al. Photovoltaic Venture Analysis. Final Report, Vol. I. Solar Energy Research Institute, U.S. Department of Energy. Contract No. EG-77-C-01-4042, July 1978.

2. U.S. Department of Energy. Photovoltaic Program. DOE/ET-0019/1, January 1978. p. 241.

3. Goldsmith, J.V., and D.B. Bickler. LSA Project Technology Development Update: Low-Cost Solar Array Project. DOE and Jet Propulsion Laboratory (JPL). DOE/JPL-1012-7, August 1978.

4. Kelly, H. Photovoltaic Power Systems: A Tour Through the Alternatives. Science, 199(10):634, February 1978.

5. Proc. IEEE Photovoltaic Specialists Conference, 13th, Washington, D.C., June 1978.

6. Bickler, D.B., B.D. Gallagher, and L.E. Sanchez. A Candidate Low-Cost Processing Sequence for Terrestrial Silicon Solar Cell Panel. Ref. 5, p. 241.

7. Pulfrey, D.L. Photovoltaic Power Generation. Van Nostrand Reinhold Co., New York, 1978.

8. Gandel, M.G., et al. Assessment of Large-Scale Photovoltaic Materials Production. U.S. Environmental Protection Agency. EPA-600/7-77-087, August, 1977.

9. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 18, 2nd ed. John Wiley & Sons, New York, 1969. p. 111.

10. Breneman, W.C., et al. Preliminary Process Design and Economics of Low-Cost Solar-Grade Silicon Production. In Ref. 5, p. 339.

11. Kapur, V.K., L. Nanis, A. Sanjurjo, and R.W. Bartlett. Novel Duplex Vapor-Electrochemical Method for Silicon Solar Cells. SRI International. Quarterly Report No. 9, Contract No. NAS-7-100-954471, February 1 - April 30, 1978.

12. Reed, W.H., et al. Development of a Process for High Capacity-Arc Heater Production of Silicon. Ref. 5, p. 370.

13. Ingle, W. Metal. Semiconductor Grade, Solar Silicon Purification Project. Motorola Report No. 2257/8. Technical Quarterly Report No. 8. JPL Contract No. 954442, December 1977.

14. Blocher, J.M., Jr., and M.F. Browning. Evaluation of Selected Chemical Processes for Production of Low-Cost Silicon (Phase II). Batelle Columbus Lab., Quarterly Progress Report No. 10, January 1 - March 31, 1978. Contract No. NAS-7-100-954339.

15. Hunt, L.P., et al. Advances in the Dow Corning Process for Solar-Grade Silicon. Ref. 5, p. 333.

16. Walfson, R.G., and C.B. Sibley. Development of Advanced Methods for Continuous Czochralski Growth. Varian Associates First Quarterly Report. JPL Contract No. 954884, January 1978.

17. Zantendy, R. Development of Low-Cost Silicon Crystal Growth Techniques for Terrestrial Photovoltaic Solar Energy Conversion. Solar Energy, 20: 249-257, 1978.

18. Gurtler, R.W., et al. Laser-Zone Growth in a Ribbon-to-Ribbon (RTR) Process. Motorola Report No. 2256/6. JPL Contract No. 954376, June 1977.

19. Christ, M.H., et al. Determination of a Definition of Solar Grade Silicon. Final Report. Monsanto Research Corporation. JPL Contract No. 954338.

20. Siltec. Growing Toward Perfect Ion. Product Information. Menlo Park, California.

21. Holden, S.C., and J.E. Fleming. Slicing of Silicon into Sheet Materials. Varian Associates. Contract No. NAS-7-100-954374, January 1978.

22. Briggs, T.M. Industrial Hygiene Walk-Through Survey Report of OCLI, November 25, 1978. National Institute of Occupational Safety and Health (NIOSH). Cincinnati.

23. Willson, R.D., and D.R. McFee. Industrial Hygiene Walk-Through Survey Report of Monsanto Commercial Products Co., Sept. 1, 1978. NIOSH. Cincinnati.

24. Briggs, T., R. Garrison, and M. Boeniger. Industrial Hygiene Walk-Through Survey Report of Motorola Inc. Semiconductor Group, November 1, 1978. NIOSH, Cincinnati.

25. Carbajal, B.G. Automated Assembly Task, Phase 1. Final Report. Texas Instruments. JPL Contract No. 9544505. October 1977.

26. Lockheed Missiles and Space Company, Phase 2, Automated Array Assembly Task IV. Low-Cost Silicon Solar Array Project. Quarterly Report No. 1. January 1978.

27. Boeniger, M. Industrial Hygiene Walk-Through Survey Report of Spectorolab, Inc., April 5, 1977. NIOSH, Cincinnati.

28. Witham, C.R. Process Development for Automated Solar Cell and Module Production, Task 4. Automated Array Assembly. MB Associates Quarterly Report No. 1. JPL Contract No. 954882, April 1978.

29. Briggs, T., et al. Industrial Hygiene Sampling Survey Report of Monsanto Commercial Products Co., July 13, 1979. NIOSH, Cincinnati.

30. International Plasma Corp. Fundamentals of Plasma-Etching. 1976.

31. Coleman, M.G., et al. Automated Array Assembly. Phase 1. Low-Cost Silicon Solar Array Project. Motorola Annual Technical Report. JPL Contract No. 954363, February 1977.

32. D'Aiello, R.V. Automated Array Assembly, RCA Laboratories, Quarterly Report No. 4. JPL Contract No. 954352, May 1977.

33. Health Effects of Solar (Photovoltaic) Energy. First Workshop. Brookhaven National Laboratory, N.Y. July 31 - August 2, 1979.

34. D'Aiello, R.V. Automated Array Assembly Phase II, RCA Laboratories, Quarterly Report No. 1. JPL Contract No. 954868, December 1977.

35. Boeniger, M. Industrial Hygiene Walk-Through Survey Report of Sensor Technology, Inc., April 5, 1977. NIOSH, Cincinnati.

36. Khemthong, S. High Efficiency, Long Life Terrestrial Solar Panel. OCLI Final Report, JPL Contract No. 954831, March 1978.

37. D'Aiello, R.V. Automated Array Assembly, RCA Laboratories Quarterly Report No. 5. JPL Contract No. 954352, October 1977.

38. Kolyer, J.M. Accelerated/Abbreviated Test Methods. Study 4 of Task 3 (Encapsulation) of the Low-Cost Silicon Solar Array Project. Eighth Quarter Progress Report. JPL Contract No. 954458, April 1978.

39. Shaughnessy, T. Design and Fabrication of Solar Cell Modules. Spire Corp. Final Technical Report. JPL Contract No. 954655.

40. Springborn Laboratories, Inc. Investigation of Test Methods, Material Properties, and Processes for Solar Cell Encapsulants. JPL Contract No. 954527, Project 6072.1, February 1978.

41. Jones, G.T. Forty kW of Solar Cell Modules for Large Scale Production. Low-Cost Silicon Solar Array Project. Final Technical Report. Sensor Technology Inc., December 1977.

42. Hamilton, A., and H.L. Hardy. Industrial Toxicology. Publishing Sciences Group, Inc. 1974. Acton, Massachusetts.

43. A Guide for Control of Laser Hazards. American Conference of Governmental Industrial Hygienists. 1976.

44. Environmental Assessment of the Domestic Primary Copper, Lead, and Zinc Industries, Vol. I. PEDCo Environmental, Inc., EPA Contract No. 68-02-1321, November 1976.

45. GTE Sylvania Chemical and Metallurgical Division, Towanda, Pa. Written Communication from C.F. Venzia to T.W. Owens, April 1979.

46. Shirland, F.A. The History, Design, Fabrication, and Performance of Cells. Thin Film Solar Cells. Advanced Energy Conversion, 6:201-221, 1966.

47. Chamberlin, R.R. and J.S Skavman. Chemical Spray Reposition Process for Inorganic Films. Journal of the Electrochemical Society. 113 (1), 1966.

48. Jordon, J.F. Thin-Film CdS/Cu_2S Cells By Chemical Spraying. U.S. Department of Energy. Final Report. Contract No. EY-76-C-04-3579. December 1976.

49. Singh, V.P. Characteristics of Cu_xS/CdS Cell on Sprayed Thin Films. In Reference 5, p. 507.

50. Shewchun, J.R., et al. Properties of Vacuum Evaporated Cu_xS Films and Solar Cells on Si, and CdS. In Reference 5, p. 378.

51. Armantrout, G.A., et al. Photovoltaic Properties of Reactively Sputtered Cu_xS Films and Reactively Sputtered Cu_xS-CdS Heterojunctions. In Reference 5, p. 383.

52. Hovel, H.J. Review Paper: Solar Cells for Terrestrial Applications. Solar Energy, 19:605-615, 1977.

53. Schock, H.W., et al. A pilot Line for the Production of Large Area Cu_xS-CdS Solar Cells. International Solar Energy Conference, New Delhi, January 1978.

54. Shea, S.P., and L.D. Partain. Heat Treatment Effects on the Minority Carrier Diffusion Lengths, Surface Recombination Velocity, and Junction Collection Factor of Cu_xS/CdS Solar Cells. In Reference 5. p. 393.

55. Agnihotri, O.P., and B.K. Gupta. Spray Deposited $Cd_{1-x}Zn_xS$ Films for Low-Cost Solar Cells. In Reference 5, p. 195.

56. Bragagnolo, J.A. Photon Loss Analysis of Thin Film CdS/Cu_2S Photovoltaic Devices. In Reference 5, p. 412.

57. Loferski, J.J., et al. Investigation of Thin Film Solar Cells Based on Cu_2S and Certain Ternary Compounds. Annual Report. January 1975. (Brown Univ., Providence, R.I.).

58. Pawlewicz, W.T., and N. Laegreid. Sputter-Deposited Materials for Photovoltaic Devices. Proc. of the ERDA Semiannual Photovoltaic Advanced Materials Program (Review Meeting). Washington, D.C., March 1977.

59. Arjona, F., et al. Proceedings 12th IEEE Photovoltaics Specialists Conf. Baton Rouge, La. 1976.

60. Armantrout, G.A., et al. Photovoltaic Properties of Reactively Sputtered CwyS Films and Reactively Sputtered CwyS-CdS Heterojunctions. In Reference 5, p. 383.

61. Barnett, A.N., et al. Achievement of 9.15% Efficiency in Thin Film CdS/Cu_zS Solar Cells. In Reference 5, p. 419.

62. Barnett, A.N., et al. Achievement of 9.15% Efficiency in Thin Film CdS/Cu_zS Solar Cells. In Reference 5, p. 419.

63. Loferski, J.J., et al. Investigation of Thin Film Solar Cells Based on Cu_2S and Certain Ternary Compounds. Annual Progress Report. NSF Grant G1-38102X. January 1975.

64. Sahai, R., D.D. Eduall, and J.S. Harris, Jr. High Efficiency AlGaAs/GaAs Concentrator Solar Cell Development. In Reference 5, p. 946.

65. Evans, D.L., and L.W. Florschuetz. Terrestrial Concentrating Photovoltaic Power System Studies, Solar Energy, 20:37-43, 1978.

66. Hammond, A.L. Photovoltaics: The Semiconductor Revolution Comes to Solar. Science, 197:445-447, July 1977.

67. U.S. Department of the Interior. Bureau of Mines. Mineral Commodity Summaries, p. 54. January 1979.

68. Environmental Assessment of the Domestic Primary Copper, Lead, and Zinc Industries, Vol. I. EPA Contract No. 68-02-1321, November 1976.

69. Briggs, T. Industrial Hygiene Walk-Through Survey Report of Varian Associates, June 7, 1979. NIOSH, Cincinnati.

70. Ewan, J., et al. GaAs Solar Cells for High Solar Concentration Applications. In Reference 5, p. 953.

71. Fan, J.C., and C.O. Bozler. High Efficiency GaAs Shallow-Homojunction Solar Cells. In Reference 5, p. 953.

72. James, L.W., H.A. VanderPlas, and R.L. Moon. High Performance GaAs Photovoltaic Cells for Concentration Applications. Final Report. Varian Associates, Inc., December 1977.

73. Barton, D.L., and L.E. Olsen. Solar Cells Based on GaP_xAS_{1-x} Compounds. In Reference 5, p. 972.

74. Walker, G.H., and E.J. Conway. Short Circuit Current Changes in Electron Irradiated GaAlAs/GaAs Solar Cells. In Reference 5, p. 575.

75. Briggs, T. Industrial Hygiene Walk-Through Survey Report of Rockwell International, June 8, 1979. NIOSH, Cincinnati.

76. Chu, S.S., T.L. Chu, and H.T. Yang. Large Area Thin Film Gallium Arsenide Solar Cells. In Reference 41, p. 956.

77. Costello, D., et al. Photovoltaic Venture Analysis. Progress Report. Solar Energy Research Inst., April 1978.

78. Dapkus, P.D., et al. The Properties of Polycrystalline GaAs Materials and Devices for Terrestrial Photovoltaic Energy Conversion. In Reference 5, p. 960.

79. Borrego, J.M., and S.K. Ghandhi. Polycrystalline Thin Film Gallium Arsenide Cells. Proceedings of the ERDA Semiannual Photovoltaic Advanced Materials Program Review Meeting. Washington, D.C., March 1977.

80. Dapkys, P.D., R.D. Dupuis, and R.P. Ruth. Rockwell International Electric Research Center. TGIN Films of GaAs on Low-Cost Substrates. Proceedings of the ERDA Semiannual Photovoltaic Advanced Materials Program Review Meeting. p. 644. Washington, D.C., March 1977.

81. Chu, S.S. Thin Films of Gallium Arsenide on Low-Cost Substrates. Proceedings of the ERDA Semiannual Photovoltaic Advanced Materials Program Review. p. 663. Washington, D.C., March 1977.

82. Yeh, Y.C., F.P. Ernest, and R.J. Stirn. Progress Towards High Efficiency Polycrystalline Thin-Film GaAs AMOS Solar Cells. In Reference 5, p. 966.

83. Fan, J.C. GaAs Thin Film Solar Cells. MIT/Lincoln Laboratory. Proceedings of the ERDA Semiannual Photovoltaic Advanced Materials Program Review. p. 593. Washington, D.C. March 1977.

84. U.S. Department of Energy. Energy Research and Development Administration. Solar Program Assessment: Environmental Factors, Photovoltaics. Environmental and Resource Assessments Branch, Division of Solar Energy, March 1977.

85. Carlson, D.E. Amorphous Silicon Solar Cells, IEEE Transactions on Electron Devices, 24 (4), April 1977.

86. Ovshinsky, S.R., and A.A. Madan. A New Amorphous Silicon-Based Alloy for Electronic Applications. Nature, Vol. 276, November 30, 1978.

87. Wilson, J.I., J. McGill, and P. Robinson. M-I-S Solar Cells on Amorphous Silicon. In Ref. 5, p. 751.

88. Anderson, W.A., J.K. Kim, and L. Hyland. Surface State and Performance Evaluation of Schottky Barrier Solar Cells on Amorphous Silicon. In Ref. 5, p. 755.

89. Carlson, D.E. Amorphous Silicon Solar Cells. RCA Engineer, April 1979.

90. Burgess, E.L. Photovoltaic Energy Conversion Using Concentrated Sunlight. Optical Engineering, 16 (3), May-June 1977.

91. Pausi, A.J. Small Business Claims Key to Cheap Solar Power, Cincinnati Enquirer, January 28, 1979.

92. Leonard, S.L.. Central Station Power Plant Applications for Photovoltaic Solar Energy Conversion. In Reference 5, p. 1190.

93. Linn, J.K., Optimization of Terrestrial Photovoltaic Power Systems. In Reference 5, p. 1166.

94. Sears, D.R., D.V. Merrifield, M.M. Penny, and W.G. Bradley. Environmental Impact Statement for a Hypothetical 1000 MWe Photovoltaic Solar-Electric Plant. EPA Contract No. 68-02-1331, August 1977.

95. Tsow, P., and W. Stolte. Effects of Design on Cost of Flat-Plate Solar Photovoltaic Arrays for Terrestrial Central Power Applications. In Reference 5, p. 1196.

96. Jones, G.J., and D.G. Schueler, Status of the DOE Photovoltaic Systems Engineering and Analysis Project. In Reference 5, p. 1160.

97. James, L.W., and J.K. Williams. Fresnel Optics for Solar Concentration on Photovoltaic Cells. In Reference. 5, p. 673.

98. Edenburn, M.W., D.G. Scheuler, and E.C. Boes. Status of the DOE Photovoltaic Concentrator Technology Development Project. In Reference 5, p. 1028.

99. Wilkening, H.A. Design of a 10 kW Photovoltaic 200/1 Concentrator. In Reference 5, p. 669.

100. Zimmerman, D.K. Evaluation of a Plastic Parabolic Concentrator for Terrestrial Photovoltaic Applications. In Reference 5, p. 680.

101. Masters, W., R. Maraschin, and W. Kennedy. A Novel Low-Cost Photovoltaic Concentrator. In Reference 5, p. 686.

102. Donovan, R.L., et al. Ten Kilowatt Photovoltaic Concentrating Array. In Reference 5, p. 1125.

103. Luque, A., et al. Project of the "Romon Areces," Concentrated Photovoltaic Power Station. In Reference 5, p. 1139.

104. Rapp, C.F., and N.L. Boling. Luminescent Solar Concentrators. In Reference 5, p. 690.

105. Wood, J.R., and J.F. Long. Performance Tests of Organic Dyes in a Planar Solar Concentrator With Ribbon Photovoltaic Cells. In Reference 5, p. 1158.

106. Accident Prevention Manual for Industrial Operations, National Safety Council, Chicago, Ill. 6th Ed. 1973.

107. Cull, R.C., and A.F. Forestier. The DOE/LeRC Photovoltaic Systems Test Facility. In Reference 5, p. 22.

108. Memo: Visit to Sandia Laboratory Solar Photovoltaics Demonstrations, from Terry Briggs, PEI, to Mark Boeniger, NIOSH. 1979.

109. Shumka, A., and K.H. Stern. Some Failure Modes and Analysis Techniques for Terrestrial Solar Cell Modules. In Reference 5, p. 824.

110. Sax, I.N. Dangerous Properties of Industrial Materials, 5th Ed. Van Nostrand Reinhold Co., New York, 1979.

111. Minutes of the Meetings of the Photovoltaics Advisory Subcommittee on Safety. Chairman, S. Forman, June 1978.

112. Young, L.L. Solar Energy Research at Sandia Laboratories and Its Effects on Health and Safety. Sandia Laboratories, Safety Eng. Div., Albuquerque, N.M., October 1977.

113. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Crystalline Silica. 1974.

114. Giles, R.D., et al. Massive Proteinuria and Actual Renal Failure in a Patient with Acute Silicoproteinosis. The American Journal of Medicine, Volume 64, February 1978.

115. Saldanha, L.F., V.J. Rosen, and H.C. Gonick. Silicon Nephropathy. The American Journal of Medicine, Volume 59, July 1975.

116. Dobbie, J.W., M.J. Gray, and A.C. Kennedy. Silicon and the Kidney. A report of the Association of Physicians of Great Britain and Ireland. November 1978.

117. American Conference of Governmental Industrial Hygienists. Documentation of the Threshold Limit Values for Substances in Workroom Air, 3rd Ed. 1976.

118. Wilson, R.K., et al. Effects of Chronic Amorphous Silica Exposure on Sequential Pulmonary Function. Journ. of Occ. Med., 21 (6), June 1979.

119. Plunkett, E.R., and B.S. DeWitt. Occupational Exposure to Hi-Sil and Silene. Arch. Environ. Health, 5:469-472, 1962.

120. Volk, H. The Health of Workers in a Plant Making Highly Dispersed Silica. Arch. Environ. Health, 1:125-128, 1960.

121. Vitrums, V.C., et al. Pulmonary Fibrosis from Amorphous Silica Dust; a Product of Silica Vapor. Arch. Environ. Health. 32:62-68, 1977.

122. Johnson, G., T.R. Lewis, and D.H. Groth. Evaluation of Health Hazard of Amorphous Silica-Coated Cristobalite Following Intratracheal Injection in Rats. NIOSH Toxicology Branch, Cincinnati. 1973.

123. Summary of NIOSH Recommendations for Occupational Health Standards. Department of Health, Education, and Welfare. NIOSH, Cincinnati.

124. Sax, I.N. Dangerous Properties of Industrial Materials. Van Nostrand Reinhold Co., New York. 1975.

125. Casarett, L.J., and J. Doull, ed. Toxicology: The Basic Science of Poisons. The MacMillan Co., New York, 1975.

126. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Carbon Monoxide, 1972.

127. Proctor, N.H., and J.P. Hughes. Chemical Hazards of the Workplace. J.B. Lippincott Company, Philadelphia. 1978.

128. Saldanha, L.B., V.J. Rosen, and H.C. Gonick. Silicon Nephropathy. The American Journal of Medicine, Volume 59, July 1975.

129. Dobbie, J.W., M.J. Gray, and A.C. Kennedy. Silicon and the Kidney. A Report of the Association of Physicians of Great Britain and Ireland. November 1978.

130. Diamond, P., and J.M. Cohen. Methyl Chloride Survey Report on Dow Corning Corp. Midland, Michigan SRI International For the Center for Occupational and Environmental Safety and Health, January 1978.

131. Union Carbide Corporation, Silane Monomers for Epitaxial Silicon. Product Information, New York, November 1970.

132. M&T Chemicals, Inc. Material Safety Data Sheet. Rahway, New Jersey.

133. Dow Corning. Material Safety Data Sheet. Midland, Michigan. March 1972.

134. Union Carbide. Material Safety Data Sheet. New York, New York.

135. Manufacturers Chemical Association, Preliminary Material Safety Data Sheet on Chlorosilanes. In press.

136. American Conference of Industrial Hygienists. TLV's for Chemical Substances and Physical Agents in the Workroom Environment With Intended Changes for 1978.

137. Key, M.M., et al., ed. Occupational Diseases: A Guide to Their Recognition. Center for Disease Control (U.S. Public Health Service), NIOSH. Publication No. 77-181, June 1977.

138. Matheson Gas Products. Material Safety Data Sheet, East Rutherford, N.J.

139. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Hydrogen Fluoride, March 1976.

140. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Exposure to Sodium Hydroxide. 1975.

141. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Trichloroethylene. 1973.

142. U.S. Department of Health, Education, and Welfare. National Cancer Institute. Carcinogenesis Technical Report Series No. 2. Carcinogenesis Bioassay of Trichloroethylene. DHEW Publication No. (NIH) 76-802, 1976.

143. Material Safety Data Sheet for Boron Trichloride. Ker-McGee Corporation, Oklahoma City, Oklahoma. June 1971.

144. U.S. Department of Health, Education, and Welfare. NIOSH Registry of Toxic Effects of Chemical Substances, Vols. I and II. 1977.

145. Goyer, R.A., and M.A. Mehlman, ed. Toxicology of Trace Elements. Hemisphere Publishing Corporation, Washington, London, 1977.

146. Monsanto Chemical Intermediates Co. Supplemental Product Information. Acute Toxicity Studies with Phosphorous Oxychlorine.

147. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Nitric Acid. March 1976.

148. Monsanto Chemical Intermediates Co. Phosphorous Trichloride and Phosphorous Oxychloride. Technical Bulletin No. 102.

149. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Xylene. 1975.

150. Schoental, R. Carcinogenic and Chronic Effects of 4,4' Diaminodiphenylmethane and Epoxy Resin Hardener. Nature Vol. 219. September 1968.

151. Hine, C.H., et al. An Investigation of the Oncogenic Activity of Two Representative Epoxy Resins. Cancer Research Vol. 18, January 1958.

152. Weil, C.S., et al. Experimental Carcinogenicity and Acute Toxicity of Representative Epoxides. Am. Ind. Hyg. J., Vol. 24, July/August 1963.

153. Dernehl, C.J. Hazards to Health Associated with the Use of Epoxy Resins. Journ. of Occ. Med., 5 (1), 1963.

154. Leong, C.J., and H.N. McFarland. Hazards from Thermo-Decomposition of Epoxy Resins. Arch. Env. Health, 7:675-682, 1963.

155. Fournier, P.E., and P. Gervais. Toxicological Study of Epoxy Resins, Occupational Health Rev. 17 (1), 1965.

156. U.S. Department of Health, Education, and Welfare. Safety and Health in Soldering and Brazing. Center for Disease Control (U.S. Public Health Service); NIOSH, Division of Technical Services. Cincinnati, September 1978.

157. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Inorganic Lead. Revised criteria, 1978.

158. Talbot, C., and A. Hricko. Hazards of the Electronics Industry. Monitor, Vols. 4 and 6, August-September 1977.

159. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Formaldehyde. December 1976.

160. Ross, W.M. Environmental Problems in the Production of Printed Circuits. Ann. Occup. 15:141-151, 1972.

161. Colligan, M.J., and W. Stockton. The Mystery of Assembly Line Hysteria. Psychology Today, June 1978.

162. Smith, M.J., M.J. Colligan, and J.J. Hurrell. Three Incidents of Industrial Mass Psychogenic Illness. Journ. of Occupational Med. 20 (6), June 1978.

163. Murphy, L.R., and M.J. Colligan, Mass Psychogenic Illness in a Shoe Factory: A Case Report. in press: International Archives of Occ. Environmental Health.

164. Colligan, M.J., et al. An Investigation of Apparent Mass Psychogenic Illness in an Electronics Plant. in press: Journ. of Behavioral Medicine.

165. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Cadmium. 1976.

166. World Health Organization. International Agency for Research on Cancer. Some Inorganic or Organometallic Compounds. Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man. Vol. 2, 1973.

167. World Health Organization. International Agency for Research on Cancer. Vol. 7, 1974. p. 95.

168. Michigan Chrome and Chemical Company, Tolber Division. Material Safety Data Sheet for Microstop^R.

169. Talbot, C., and A. Hricko. Hazards of the Electronics Industry, Monitor, Vol. 4, and 6, August-September 1977.

170. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Methylene Chloride. March 1976.

171. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Toluene. 1974.

172. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Hydrogen Sulfide. May 1977.

173. Goldblatt, M.W., and J. Goldblatt. Industrial Carcinogenesis and Toxicology. Part I: Occupational Carcinogenesis. In Industrial Medicine and Hygiene, Vol. 3. Butterworth, London, 1956. p. 210-215.

174. Buchanan, W.D. Toxicity of Arsenic Compounds. Elsevier Amsterdam, 1962.

175. U.S. Department of Health, Education, and Welfare. Public Health Service. Drinking Water Standards. 1962.

176. U.S. Department of Health, Education, and Welfare. NIOSH Registry of Toxic Effects of Chemical Substances, Vol. I and II. 1976.

177. U.S. Department of Health, Education, and Welfare. NIOSH Criteria for a Recommended Standard for Occupational Exposure to Sulfuric Acid. 1974.

178. American Conference of Governmental Industrial Hygienists. Industrial Ventilation, A Manual of Recommended Practice. 15th Edition. 1978.

179. U.S. Department of Labor, Occupational Safety and Health Administration, Occupational Exposure to Inorganic Arsenic. Federal Register, Vol. 43, No. 88. May 1978. p. 19584.

APPENDIX

The appendix includes the trip reports covering visits to 14 plants producing solar cells or materials used in the production of solar cells. The plants, designated as A through N, are ordered by type of process technology as follows:

- Plants A through I: Single-crystal silicon technology
  - Plant A - Chlorosilane production
  - Plants B through D - Ingot and wafer production
  - Plants E through I - Module production

- Plant J: Amorphous silicon research and development (R&D)

- Plants K and L: Cadmium sulfide R&D

- Plants M and N: Gallium arsenide R&D

Each report describes the plant and its processes, the work force, and the medical, health, and safety program and summarizes the findings.

Initial walk-through surveys of Plants B, E, and K were followed by indepth sampling surveys. The sampling included personal and area samples as well as ventilation measurements. The trip reports for these facilities include results of the sampling surveys.

The following is an alphabetical listing of the 14 facilities visited. They are listed in this manner to protect the proprietary aspects of some of the information presented.

ARCO Solar, Inc., Chatsworth, California
Dow Corning Corporation, Hemlock, Michigan
Monsanto Commercial Products Company, St. Peters, Missouri
Motorola, Inc., Phoenix, Arizona
Optical Coating Laboratory, Inc., City of Industry, California
Photon Power, Inc., El Paso, Texas
RCA/David Sarnoff Research Center, Princeton, New Jersey
Rockwell International, Thousand Oaks, California
SES, Inc., Newark, Deleware
Siltec Corporation, Menlo Park, California
Solar Power Corporation, North Billerica, Massachusetts
Solarex Corporation, Rockville, Maryland
Union Carbide Corporation, Sistersville, West Virginia
Varian Associates, Palo Alto, California

PLANT A: CHLOROSILANE PRODUCTION FACILITY
WALK-THROUGH SURVEY

SUMMARY OF SURVEY FINDINGS

Plant A produces chlorosilanes, principally trichlorosilane, with metallurgical-grade silicon and hydrochloric acid (HCl) as raw materials. This is a fully automated continuous operation. Powdered silicon and HCl react to form chlorosilanes, which are subsequently fractionated into pure components. Hydrogen formed in the reaction is vented to the atmosphere after cooling. The principal industrial hygiene concerns are the chlorosilanes, which are corrosive, decompose in air, and release HCl.

The major industrial hygiene concerns involve accidental release of chlorosilanes (and thus HCl) and maintenance procedures. Generally the operation appeared well designed and required very little intervention, thus minimizing any routine exposures.

PLANT DESCRIPTION

This facility, which produces a wide range of silicones, uses chlorosilanes as a starting material and offers them for sale. The chlorosilane facility, a part of the monomers plant, has been in operation since 1955.

Except for feed silicon grinding, all processing steps are located outside. Trichlorosilane is the major product; dichlorosilane and silicon tetrachloride are also produced.

DESCRIPTION OF WORK FORCE

Six process operators per shift work on this process on a part-time basis. About 150 plant operators are represented by the International Chemical Workers Union. Approximately 10 percent of this total are women.

MEDICAL, HEALTH, AND SAFETY PROGRAM

A complete employment and medical history is maintained on each employee. Also, complete physical examinations are performed at the time of hiring and periodically thereafter; the frequency depends upon worker age.

A full-time safety director and an industrial hygienist are employed at this facility. Additionally, an industrial nurse is employed full-time; a physician is on call and works 1 day per week at the plant.

Employees must wear protective clothing, including goggles and hard hats, in the plant area. Rubber gloves are required for sampling. Special protective clothing and equipment are provided as necessary for any potentially hazardous operation.

The only lost-time accident associated with chlorosilane production in the last year was the burning of a maintenance man by chlorosilane released from a chlorosilane storage tank, which blew a rupture disc. The burns were caused by HCl, formed as a decomposition product of the released chlorosilane.

PRODUCTION PROCESSES

The chlorosilane production process consists of four stages: raw material handling, reactor section, fractionation section, and storage and distribution.

Raw Material Handling

The two raw materials, metallurgical-grade silicon and HCl, are received and processed before charging to the reactors.

Silicon is received in chunk form in enclosed rail cars, which are unloaded in an enclosed conveyor and bucket elevator, vented to a baghouse. The chunk silicon goes to a storage hopper. It is fed to grinders that reduce the size. The grinders are vented to a baghouse. The ground silicon is conveyed to storage hoppers. On-off radioactive weight indicators are used on the hoppers. The silicon is then fed to the reactor system from the storage hopper.

All portions of the transport and grinding system are enclosed or provided with local exhaust ventilation. Dust takeoffs are located at specific transfer points. Exhaust air from the system is passed through a baghouse collector, which is automatically cleaned by reverse air jet.

Hydrochloric acid comes either in rail tank cars or from internal sources. Procedures for utilization of process HCl were not reviewed in the survey.

Reactor Section

The reaction of HCl and silicon occurs in the reaction system under heat and pressure.

The reactor outlet goes to common condensers to separate the chlorosilane from hydrogen, which is also produced in the reaction. Noncondensibles then pass through a vent scrubber located at ground level.

The reactor section is provided with unenclosed platform access. The effluent condensers are located on the top reactor level.

The vent scrubber is a vertical countercurrent water scrubber open at the top to release the outlet gas stream. Because chlorosilanes decompose readily in water, this scrubber acts to remove any chlorosilanes and HCl in the noncondensible stream. The scrubber water goes to neutralization and treatment in the wastewater system. Hydrolyzed chlorosilane forms an HSiOSiH lattice.

Fractionation Section

A series of fractionators separate the mixed chlorosilanes into pure products. Trichlorosilane, the main product, is purified during this fractionation process.

The columns are provided with an unenclosed support structure. The receivers for each column are vented to a water scrubber similar to the reactor noncondensible vent scrubber.

Storage and Distribution

Pressure vessels equipped with relief devices provide intermediate storage before fractionation and product storage for each chlorosilane. These are located in a separate diked area.

Chlorosilanes are transported entirely by tanker truck. The tanker trucks and loading procedures reportedly meet or exceed Department of Transportation (DOT) requirements. Specially designed tankers with internal shutoff valves are used.

SURVEY OBSERVATIONS

Raw Material Handling

The local exhaust system was well designed and reportedly was maintained and checked on a regular monthly basis. Some problems reportedly exist in regard to duct erosion at elbows. Dust leaks were usually detected by observations of "dustiness" in the air and reportedly are repaired immediately.

Silicon dust was observed in relatively slight accumulations throughout the building. Somewhat heavy accumulation was noted around the collector box below the baghouse hopper. This reportedly resulted from spillage during changes of the collector box.

Airborne silicon dust constitutes the primary industrial hygiene concern for this area. Personal air sampling reportedly has been conducted, with results generally ranging from 5 to 8 mg/m^3, total dust. Respirable fractions have not been determined, but plans reportedly have been made to do so.

The potential health hazard from HCl was considered to be minimal, with few opportunities for exposure and very limited personnel interaction with the process equipment. Physical hazards for maintenance and plumbing operations were more significant, and appropriate personal protective equipment was reportedly in use.

Reactor and Fractionation Sections

Use of pumps and valves is minimized in the reactor process area to minimize corrosion, maintenance problems, and exposure potential.

The hazard of hydrogen fire was well recognized. It was noted that any hydrogen fire would be visible ("smokey") because of chlorosilane contamination of the vent stream. Reportedly, any fire that might arise could be "snuffed out" immediately by nitrogen purge of the vent.

The primary industrial hygiene concern throughout chlorosilane processing and storage would be exposure to HCl, which would only be expected during maintenance or process accidents, such as formation of an HCl vapor cloud. Written procedures and employee training were reportedly quite thorough in regard to a "cloud alert" procedure.

Personal air sampling has reportedly been conducted for background HCl around the process equipment. Levels typically have been less than 1 ppm. Somewhat high levels have been found during certain maintenance operations.

Storage and Distribution

No significant hazards were noted, except for HCl resulting from accidental leakage.

COMMENTS

The process appeared well designed and maintained and highly automated, requiring little operator intervention. Also the industrial hygiene program was well developed, covering major health and safety considerations. Thus industrial hygiene concerns of this facility were not regarded as serious and would not warrant followup with an in-depth survey. Potential hazards from silicon dust and HCl were generally well controlled. Personnel were aware of the potential hazards and had conducted air sampling to verify low levels. Safety and health strongly appear to take precedence over process and manufacturing demands, as stated by plant and corporate personnel.

PLANT B: SILICON WAFER PRODUCER-- SAMPLING SURVEY

INTRODUCTION

A walk-through survey was conducted at this plant on September 1, 1978. Plant B was chosen for an in-depth survey because it is a commercial producer of silicon wafers and also of gallium arsenide wafers. Although these materials are used primarily in the semiconductor industry, most of the production steps are similar to processes that would be used for photovoltaic materials.

PLANT DESCRIPTION

Plant B produces electronic and solar grade silicon by the Czochralski (Cz) and Zone Refining techniques, polycrystalline silicon by the Siemens process, and partially finished and finished light-emitting diodes and displays of gallium arsenide (GaAs) and gallium arsenide phosphide (GaAsP). The operations of interest take place in six buildings. A small percentage of the silicon produced at this facility is for photovoltaic solar cells.

The facility was designed to produce high-purity silicon for the electronics industry, and has been in operation since 1960. The total number of employees is now more than 1000. About half of the production employees are female. Workers are not unionized.

Silicon for solar applications is processed only in the crystal pulling, slicing, and crest cleaning areas of the plant.

DESCRIPTION OF PROCESS: POLYCRYSTALLINE SILICON

Plant B produces polycrystalline silicon by the Siemens process, in which a thin seed rod of single crystal silicon is electrically heated inside a 10-m^3 (350-ft^3) quartz bell jar (decomposition reactor). A controlled amount of trichlorosilane (TCS) and hydrogen is fed into the jar. The TCS is decomposed at approximately 1160°C (1890°F) in the presence of hydrogen, forming polycrystalline silicon, hydrogen chloride, and silica. Depending on the size of the polycrystalline silicon rod desired, the cycle time may be longer than 100 hours. More than 20 decomposition reactors are now in use. The waste streams from the process contain hydrogen and hydrogen chloride (which are recovered for use in the process) and silica (which is stated to be amorphous).

Leaks in the hydrogen system are detected throughout the decomposition reactor area by 18 hydrogen detectors (Bacharach Model CD830P) and are set to alarm at 10 percent of the lower explosive limit. It is stated that sufficient ventilation is maintained in the area to prevent formation of an explosive hydrogen-air mixture and that the hydrogen detectors are calibrated monthly.

The resident industrial hygienist has monitored for TCS using hydrogen chloride detector tubes, and has only found traces of TCS inside the quartz bell jars after a reactor has been opened.

The reactor design includes safety devices that shut the process down if the pressure drops, because a cracked or leaking bell jar will waste the feed materials.

Respirators are not required in any part of the polycrystalline production area, but self-contained breathing apparatus and hoseline masks are available for use in an emergency situation.

Hydrogen chloride corrosion was seen on exposed metal walls in the polycrystalline area, but it was stated that HCl tube type grab samples in the general area show nondetectable levels. These tubes, however, have a sensitivity to 1 ppm only. Time-weighted average (TWA) measurements for HCl are now being taken in this area.

DESCRIPTION OF PROCESS: ZONE REFINING

One method used to convert polycrystalline ("poly") silicon to single crystal form is the zone refining (ZR) technique. A poly rod is heated by radio frequency (RF) energy in an annular ring, attached to a single crystal seed rod, and drawn through the RF annulus at a controlled rate. The narrow zone on either side (above and below) the annulus is a zone of molten silicon, which solidifies (when it is out of the heated zone) into a single crystal about the seed. The poly rod is first passed through the ZR furnace in an argon atmosphere to convert it to a single crystal structure. It is then passed through a second ZR furnace, into which doping gases are introduced within the molten silicon zone to impart desired electrical properties to the silicon. The dopants are phosphine (to produce "n" type, or electron-rich silicon) and diborane (to produce "p" type, or electron-poor silicon). They are introduced into the ZR furnace in concentrations of 50 to 500 ppm in the argon atmosphere. The ZR furnaces operate at less than 690 kPa (100 psi) gauge pressure, and their control cabinets are exhausted to purge any diborane or phosphine leaks.

The phosphine and diborane are stored in a locked vault outside the ZR furnace area, the door of which has a timed locking system so that the air in the gas bottle storage room is purged for 5 minutes before a workman enters to service the bottles. Bottles are changed about once a month, and a Draeger tube sample is taken through a sampling port after the 5-minute purge and before a worker enters the room. The operation, which is rigidly controlled, must be done by two workers wearing air-supplied hose masks. Because phosphine is heavier than air, vents are located at floor level to enhance the effectiveness of the purge cycle.

PROCESS DESCRIPTION: CRYSTAL CLEANING

Rods of poly silicon blast are cleaned in this area by shot blasting with alumina. Grain boundaries are visually inspected for undesirable characteristics. The surface is etched and cleaned in a hooded acid dip tank using an acid mixture common in the electronics industry (57% nitric acid, 18% hydrofluoric acid, and 25% acetic acid), acetone, chromic acid, and hydrofluoric acid. The hood is stated to have a face velocity of at least 33-M (100 ft) per minute. J.T. Baker spill cleanup kits for hydrofluoric acid (HF), flammable solvents, caustics, and acids are located next to the hood area.

PROCESS DESCRIPTION: GRINDING DEPARTMENT

Although this area was visited next, it involves operations to prepare the poly rods for zone refining. The poly rods are surface ground using wet centerless grinders to give a smooth outer surface prior to zone refining. Zone-refined rods are then returned to this area for x-ray crystallography to determine the crystal orientation before the rods are sliced into individual silicon wafers. All employees exposed to x-rays wear thermoluminescent dosimeter rings to document their individual exposures. The average annual dose is reported to be approximately 17 millirems (mrem), compared to an allowable 75,000 mrem/year for an extremity.

The resident industrial hygienist performs a survey once a week for alpha radiation, using a Victoreen 490 for beam measurements and a Victoreen 440 for scattered radiation. The levels found are reported to be consistent with the expected background levels.

The single crystal rods from the ZR process are returned to this area, x-rayed, and then ground flat on one side prior to slicing. Particulate samples are taken in this area using matched weight cassettes to monitor respirable dust. Concentrations from 8-hour samples are reported to be less than 0.1 mg of respirable dust.

Another potential radioactive source in this area is phosphorous 32, which may be present on single crystal rods that are subjected to neutron transmutation doping (NTD) by an outside contractor. In the NTD process, individual silicon atoms are transmitted to phosphorous atoms, thus eliminating the phosphine doping step. The contractor is required to clean and etch the rods before shipment, and they are given an incoming inspection in this area using an Eberline MS-2 miniscaler and a PAC 4G survey meter. The plant acceptance limit on NTD rods is 2 microcuries per gram of material; any rods in excess of this limit are returned. The company is licensed by the Nuclear Regulatory Commission to handle exempt quantities of NTD materials. The State of Missouri licenses the x-ray diffraction units. Affected employees are given an x-ray exposure summary annually, and it becomes a part of their medical files.

PROCESS DESCRIPTION: CZOCHRALSKI CRYSTAL PULLING

The Czochralski process is the other method used in the plant to produce single crystal silicon. In this process, silicon rods are broken into chunks, melted to liquid form in a resistance-heated quartz crucible inside a vacuum furnace, and grown into a single crystal rod of up to 10.2 cm. (4-in.) diameter by dipping a seed crystal into the melt and withdrawing it at a controlled rate. Doping materials (e.g., boron, red phosphorous, antimony) are added to the melt in the form of small pieces of previously doped rods so that the resulting dopant concentration is in the parts-per-million range. The reported hazards in this area are acid burns and silicon splinters.

PROCESS DESCRIPTION: CRYSTAL PULLING LABORATORY

In this area, the ends of the Cz-grown rods are etched with chromic acid and hydrofluoric acid for evaluation and bulk resistivity measurements; then the exterior of the rod is etched in enclosed, vented, cabinet-style hoods with the mixed etchant (57%, 18%, 25%) mentioned above. This is essentially a chemical machining process to prepare the rod for slicing. The rod is etched, rinsed, and put through an air drying cycle. The spent acid is used only once and is then neutralized in the water treatment plant. All employees in the etching area wear Tyvek smocks and safety glasses with side shields. All acids are delivered to this and other areas of the plant by gravity feed.

PROCESS DESCRIPTION: SLICING DEPARTMENT

The single crystal rods are epoxy bonded along their flat surface to a carbon holder and are then sliced with a diamond coated circular saw. The slices are placed in trays of methylene chloride, which is covered with water to reduce solvent evaporation. The coolant water used in the slicing operation contains small amounts of a biocide and a fungicide. The noise in this area was reported to be in the range of 78 to 81 dBA.

PROCESS DESCRIPTION: CLEANING AREA

The area adjacent to the slicing department contains an ultrasonic vapor degreaser in which the slices are cleaned in a mild soap solution, dilute potassium hydroxide, methanol, and, finally, a dip in a Freon degreaser.

The ultrasonic cleaning stations have chiller vapor barriers and slotted hoods over each tank. The Freon degreaser has reportedly been measured and exhibits Freon concentrations of 15 ppm or less.

PROCESS DESCRIPTION: LAPPING DEPARTMENT

The slices are surface lapped on one or both surfaces with a microgrit compound consisting of calcined aluminum oxide, ethylene glycol, and water.

PROCESS DESCRIPTION: SLICE ETCHING

In this area, the slices are etched to final desired thickness using the same mixed acid etchant in acid hoods. Oxides of nitrogen are known to evolve from the slice being cleaned, and it is reported that colorimetric indicator tube samples taken in the area have shown essentially no exposure (the typical minimum detectable limit is 0.5 ppm). The hoods are reported to have face velocities of at least 82 m (250 ft) per minute. The fumes from this operation are passed through an NO_2 scrubber and exhausted to the air. All workers in the area are required to wear gowns, glasses, or face shields. The room is totally enclosed and has no backup fume removal system to be used in the event of a power failure.

PROCESS DESCRIPTION: POLISHING AREA

Slices from the final etching operation are cleaned in a vapor degreaser with a mixture of half Freon TF and half methylene chloride. Prior to lap polishing, the slices are attached to round lapping plates with a mixture of trichloroethylene in wax. This operation is carried out in front of slotted hoods, and it is reported that monitoring for trichloroethylene has found levels of between 40 and 50 ppm. The slices are then lap-polished with Ludox, a DuPont amorphous silica polishing compound. Dust samples in this area have been reported to be below 0.1 $\mu g/m^3$ of total dust. This operation is required for semiconductor grade wafers but is not necessary for photovoltaic applications.

PROCESS DESCRIPTION: CLEANING, INSPECTION, PACKAGING

The lap-polished slices are cleaned in hot dilute nitric and sulfuric acids, then in a series of cascades of hydrofluoric acid and ammonium hydroxide. They are given a final Freon wash, after which they are mechanically scrubbed and spun until dry. The finished cells are sealed in cans under nitrogen. These operations are automated and appeared to present a low worker health hazard.

PROCESS DESCRIPTION: PRODUCTION OF GaAs AND GaAsP LIGHT-EMITTING DIODES (III-IV AREA)

This area produces a completely separate product line: finished and semifinished light-emitting diodes for such applications as calculators and displays. Although the materials made here are not used for photovoltaic purposes (except for experimental and spacecraft applications of GaAs photovoltaic cells), a walk-through survey was conducted.

The gallium arsenide phosphide (GaAsP) is grown in much the same manner as Siemens process silicon--doped with arsine and phosphine, sliced, and polished. An epitaxial layer is deposited on the surface in a chamber, then conventional photographic masking techniques are used to mask a desired circuit pattern on the slice.

The arsenic levels in the III-IV production area are reported to be approximately 1.7 $\mu g/m^3$. Ambient air samples have been taken for EPA purposes, but no numbers were available.

Gallium arsenide is made in resistance-heated furnaces by the gradient freeze method, using electronics grade arsenic of 99.999999 percent purity. A danger of arsenic trioxide formation in the furnaces may occur if the equipment malfunctions. Gradient freeze cells are reported to explode once or twice every 4 or 5 months. An alarm system senses any out-of-limits condition, and after a waiting period a cleanup crew enters in protective clothing and self-contained breathing apparatus to vacuum any spilled arsenic or arsenic trioxide. Each gradient freeze furnace is under a negative pressure and exhausts about 3.5 m^3/min (125 ft^3/min).

POSITIVE FINDINGS

The company recognizing that losses for sick time extend beyond the workplace, addresses the total health and safety status of the individual. This helps to assure that health-related changes will be recognized.

Pre-employment and periodic medical examinations are conducted and include the principal aspects which are usually recommended,

General medical history

Physician's "hands on" evaluation

Blood tests

Sight screening

Hearing screening

Qualified industrial hygiene personnel are available, both locally and at corporate headquarters, to evaluate individual situations. A nurse is in the plant for daily first aid and general health counseling.

The principal potential health hazards appear to be controlled by a well planned program. Usage and applications of hazardous materials are documented and monitored.

NEGATIVE FINDINGS

A decentralized management structure puts the responsibility for worker health totally on plant personnel. Corporate industrial health and safety personnel do not appear to offer an adequate audit or overview function. Recognition, evaluation, and control are thus limited to knowledge and experience available at the plant level. The medical program is limited to general industrial health. It does not take advantage of opportunities for detection and assessment of health conditions related to more specific types of exposure, such as:

Hypersensitivity to arsenic, gallium, organic solvents, and other materials.

Lung function impairment, either pre-existing or caused by exposure to NO_x, HCl, HNO_3, or phosphine.

Skin exposure or contact with solvents, acids, alkalies, etc.

The stress that is related to 7-day rotating shifts is not being fully addressed. Recent studies have indicated a greater incidence of accidents and psychological problems from such schedules. No formal program of ventilation control appears to be in operation.

SURVEY PROCEDURES

Air samples were collected to evaluate worker exposure to particulates and silica in the areas of the Siemens process, ingot growing, ingot cropping and rounding, and wafer slicing. Samples were collected and analyzed for hydrofluoric acid mist in the ingot and wafer etching areas. Samples were also collected for nitrogen oxides (NO, NO_2) in the wafer etching area. Solvent exposure was monitored in the wafer cleaning area. The gallium arsenide processing area was sampled for As exposure.

Brief descriptions of the techniques used to collect and analyze the air samples obtained during the survey are summarized below.

Particulate Samples

All particulate air samples, both personal and area, were obtained by drawing air at a flow rate of about 2 liters per minute through standard closed-face PVC filter cassettes. Mine Safety Appliances Model G or Bendix closed-face BDX 55HD personal sampling pumps were used. For personal samples, pumps were attached to the worker's belt, and the sampling tubes were clipped in a vertical position to his lapel or shirt collar. Some filter cassettes were changed halfway through the shift while others, particularly area samples, were obtained during the full shift. Some short-term peak exposure samples were collected, particularly during cleanup operations.

Selected particulate samples were also analyzed for total silica (SiO_2) and crystalline α-quartz. Total SiO_2 was determined colorimetrically using NIOSH method P&CAM 106; the crystalline α-quartz fraction was determined by x-ray diffraction using NIOSH analytical method P&CAM 109.

Hydrogen Fluoride

Hydrogen fluoride air samples were collected in the ingot and wafer etching work areas. Two collection methods were used: impregnated filters and HF bubblers. In the impregnated filter method, PVC filters were soaked in a sodium acetate solution, then air-dried and assembled in closed-face filter cassette units. The sampling method followed was similar to that used for particulate sample collection presented above. This is an unpublished sample collection method. The HF bubbler method consisted of drawing at about 1 liter per minutes through a midget bubbler containing 10 ml of 0.1 N sodium hydroxide to trap HF.

Analysis of impregnated filters consisted of soaking filters in water followed by ultrasonic agitation for 15 to 30 minutes to complete the removal of sodium fluoride on the filter and bring into solution. The water solution was then analyzed using a fluoride ion specific electrode.

Bubbler solutions were diluted to a standard volume and analyzed using fluoride ion specific electrode. This procedure follows NIOSH analytical method S176.

Nitrogen Dioxide and Nitric Oxide

Samples were collected in the wafer etching area for nitrogen dioxide (NO_2) and nitric oxide (NO) exposures. Air samples were collected by drawing air at a rate of about 100 cm^3/min through special solid sorbent tubes using SKC low-volume pumps. Collected samples were capped and kept in a freezer upon return to the laboratory. In the three-section sorbent tubes used, NO_2 is absorbed in the first section. The NO present is converted to NO_2 in the second section and the NO_2 thus formed is absorbed in the third section.

Samples were analyzed using NIOSH analytical method P&CAM 231. The first and third sections of the sorbent are desorbed with solutions of TEA in water and the nitrite in these solutions is determined spectrophotometrically by the Griess-Saltzman reaction. The nitrite found in the first section is reported as NO_2 and the nitrite in the third section is reported as NO.

Arsenic

Personal and area samples were collected in the GaAs production area for arsenic exposure. Samples were collected using cellulose membrane filter cassettes by a method similar to that described above for particulate samples.

In the PEDCo Environmental laboratory, samples were analyzed for arsenic using NIOSH analytical method S309. In this procedure, the sample-containing filters are ashed using nitric and perchloric acids to destroy the filter and other organic materials in the sample. The solutions of arsenic in nitric acid and standards are pipetted into the graphite furnace of an atomic absorption spectrophotometer. An electrodeless discharge lamp for arsenic is used. The absorbance is proportional to the arsenic concentration.

Solvent Cleaning

The wafer cleaning area was sampled for solvent exposure. The solvents contained trichlorotrifluorethane (TCF) and isopropanol (IPA). Personal air samples were collected by drawing air at a rate of about 100 cm^3/min through standard charcoal tubes using SKC low-volume pumps. The pumps were attached to the worker's belts and the sampling tubes (in holders) were clipped in a vertical position to the lapel or shirt collar. Collected samples were capped and kept in a freezer upon return to the laboratory.

In the laboratory, samples were analyzed using NIOSH analytical methods S328 for TCF and IPA. In this procedure, the charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide. An aliquot of the desorbed samples is injected into a gas chromatograph. The area of the resulting peak is determined and compared with the areas obtained from the injection of standards.

RESULTS AND DISCUSSION

The results of personal and stationary air samples and ventilation measurements obtained during the survey are discussed below. Tables B-1 to B-10 present the sample results. Tables B-1 to B-3 give particulate sampling results for the Siemens process, Czochralski ingot growing, and ingot cropping and rounding work areas respectively. Table B-4 gives HF sampling results from the ingot etching area. Table B-5 gives particulate sampling results for the wafer slicing area. Tables B-6 and B-7 summarize respective sampling results for HF and nitrogen oxide

(NO and NO_2) collected in the wafer etching area. Solvent exposure results are presented in Table B-8 for wafer cleaning. Tables B-9 and B-10 present results for arsenic sampling collected in the GaAs work area. The sampling results are discussed below for each process area in which samples were collected. For cases in which samples were changed in a work area during the shift, the time-weighted-average (TWA) exposure is calculated. Table B-11 summarizes the sampling results.

Siemens Process

Airborne particulate samples collected in the Siemens process area show very low concentrations, with the highest result being 0.11 $\mu g/m^3$ for an area sample collected in the control room. The only exposures of potential concern are to trichloroethane (TCE), which is used as a solvent to clean bell jar surfaces before runs. This is a short-term exposure and is at least partially controlled by ventilation between the bell jar and outer wall that removes solvent vapors. Exposure could be reduced if the worker avoided standing over the surfaces being cleaned. No samples were collected during this cleaning operation because of its infrequency.

In general, this area appeared well controlled. Accidental release of chlorosilane, HCl, or hydrogen was the main potential problem. The control system seemed, however, to be very tight.

Czochralski Ingot Growing

Table B-2 summarizes particulate air sampling results for the Czochralski ingot growing area. Again, very low particulate exposures were found during normal operation. Two full-shift particulate exposure samples showed 0.26 and 0.25 mg/m^3; corresponding area samples taken in the respective operator work areas resulted in 0.13 and 0.15 mg/m^3 concentrations. Short-term particulate samples collected during an ingot grower cleaning cycle showed concentrations in the same range as normal full-shift exposures. For one of the full-shift personal samples, the total silica (SiO_2) level was 0.06 mg and the crystalline quartz was below the detectable limit of 0.01 mg/m^3. Analysis of a wipe sample collected from the inside on an ingot grower during cleaning showed the particulate to be 12 percent total SiO_2, but the crystalline quartz to be less than 1 percent.

This work area appeared very well controlled, and no significant industrial hygiene problems were found. Particulate control during the ingot grower cleaning cycle was excellent.

TABLE B-1. SAMPLING SUMMARY SHEET: PHOTOVOLTAIC PLANT SURVEY

Sampling for particulates

PLANT: B

Process or area:
Siemens process

Date 1979	Sample No.	Sample description	Time		Sample volume, liters	Total weight, mg	Concentration	
			Start	Stop			mg/m^3	Estimated TWA, mg/m^3
4-10	1	Personal sample: during cleaning of a unit	10:33	11:40	134	0.01	0.07	
4-10	2	Area sample: 10 ft from battery of Siemens units	9:32	16:00	776	<0.01	<0.02	
4-11	32	Area sample: between units	8:19	16:23	968	0.03	0.03	
4-11	33	Area sample: in control room	8:21	16:23	964	0.11	0.11	

TABLE B-2. SAMPLING SUMMARY SHEET: PHOTOVOLTAIC PLANT SURVEY

PLANT: B

Sampling for particulates

Process or area:
Czochralski ingot growing

Date 1979	Sample No.	Sample description	Time		Sample volume, liters	Total weight, mg	Concentration	
			Start	Stop			mg/m^3	Estimated TWA, mg/m^3
4-10	3	Personal sample: Cz operator Total SiO_2 Crystalline α-quartz	9:09	15:31	804	0.21 0.05 <0.01	0.26 0.06 <0.01	
4-10	12	Cz growing area: location near operator of sample No. 3	9:11	15:31	800	0.10	0.13	
4-11	18	Personal sample: Cz operator	8:45	15:45	840	0.21	0.25	
4-11	19	Cz growing area: location near operator in Sample 18	8:45	15:45	840	0.13	0.15	
4-11	36	Personal sample: Cz operator during grower cleaning	11:46	12:13	54	<0.01	<0.19	
4-11	37	Cz unit area sample: location near operator in Sample 36	11:44	12:13	54	0.01	0.19	
4-11	17	Wipe sample taken on inside of Cz unit during cleaning Total SiO_2: 12% Crystalline α-quartz: <1%	15:45					

TABLE B-3. SAMPLING SUMMARY SHEET: PHOTOVOLTAIC PLANT SURVEY

PLANT: B

Sampling for particulates

Process or area:
Ingot cropping and rounding

Date 1979	Sample No.	Sample description	Time		Sample volume, liters	Total weight, mg	Concentration	
			Start	Stop			mg/m^3	Estimated TWA, mg/m^3
4-10	4	Personal sample: ingot cropping operator	9:47	15:46	718	0.17	0.24	
		Total SiO_2				0.04	0.06	
		Crystalline α-quartz				<0.01	<0.02	
4-11	20	Personal sample: ingot cropping operator	8:27	15:42	818	0.28	0.34	
4-10	5	Personal sample: ingot rounding operator	9:02	15:54	824	0.20	0.24	
		Total SiO_2				0.04	0.05	
		Crystalline α-quartz				<0.01	<0.01	
4-11	21	Personal sample: ingot grinding (flat) operator	8:34	15:35	876	0.19	0.22	
		Total SiO_2				<0.01	<0.01	
		Crystalline α-quartz				<0.01	<0.01	

TABLE B-4. SAMPLING SUMMARY SHEET: PHOTOVOLTAIC PLANT SURVEY

PLANT: B

Sampling for HF

Process or area:
Ingot etching

Date 1979	Sample No.	Sample description	Time		Sample volume, liters	Total weight, mg	Concentration	
			Start	Stop			mg/m^3 (ppm)	Estimated TWA, mg/m^3 (ppm)
4-10	14	Personal sample: ingot etching operator	9:49	14:08	518	289	0.56 (0.81)	
4-10	16	Ingot etching area sample near Sample 14 operator	14:09	15:47	196	677	3.45 (5.00)	
4-11	30	Personal sample: ingot etching operator	8:29	12:08	476	247	0.58 (0.84)	
4-11	41	Same operator as Sample 30	12:08	15:42	389	263	0.68 (0.99)	0.63 (0.91)
4-11	31	Ingot etching area sample near Unit 63 - 5 ft high	8:25	11:46	410	352	0.86 (1.25)	
4-11	42	Area sample at same location as Sample 31	11:47	15:44	437	378	0.86 (1.25)	0.86 (1.25)

TABLE B-5. SAMPLING SUMMARY SHEET: PHOTOVOLTAIC PLANT SURVEY

PLANT: B

Sampling for particulates

Process or area:
Wafer slicing

Date 1979	Sample No.	Sample description	Time		Sample volume, liters	Total weight, mg	Concentration	
			Start	Stop			mg/m^3	Estimated TWA, mg/m^3
4-10	6	Personal sample: ingot slicing operator	8:50	15:39	818	0.28	0.34	
		Total SiO_2				<0.01	<0.01	
		Crystalline α-quartz				<0.01	<0.01	
4-11	22	Personal sample: ingot slicing operator	9:34	14:04	540	0.28	0.52	
		Total SiO_2				0.06	0.11	
		Crystalline α-quartz				<0.01	<0.02	
4-11	23	Ingot slicing area sample near Sample 22 operator	9:07	16:02	830	0.30	0.36	

TABLE B-6. SAMPLING SUMMARY SHEET: PHOTOVOLTAIC PLANT SURVEY

PLANT: B

Sampling for HF

Process or area:
Wafer etching

Date 1979	Sample No.	Sample description	Time Start	Time Stop	Sample volume, liters	Total weight, mg	Concentration mg/m^3 (ppm)	Concentration Estimated TWA, mg/m^3 (ppm)
4-10	8	Personal sample: wafer etching operator, HF filter	9:38	15:45	749	18.9	0.03 (0.04)	
4-11	25	Personal sample: wafer etching operator, HF filter	9:45	11:56	275	9.2	0.03 (0.04)	
4-11	39	Personal sample: remainder of shift for operator, Sample 25	11:56	15:55	502	1.77	0.35 (0.51)	0.24 (0.35)
4-11	27	Wafer etching area: midroom HF filter	8:55	11:58	375	6.3	0.02 (0.03)	
4-11	40	Wafer etching area: continuation of Sample 27	11:58	15:55	486	5.9	0.01 (0.02)	0.01 (0.02)
4-11	43	Wafer etching: area beside Sample 40, HF bubbler	14:29	15:56	183	4.7	0.03 (0.04)	
4-12	44	Personal sample: wafer etching operator, HF filter	9:10	14:05	552	332	0.60 (0.87)	
4-12	45	Wafer etching area: midroom, HF filter	8:32	14:08	810	6.7	0.01 (0.01)	

(continued)

TABLE B-6 (continued)

Date 1979	Sample No.	Sample description	Time		Sample volume, liters	Total weight, mg	Concentration	
			Start	Stop			mg/m^3 (ppm)	Estimated TWA, mg/m^3 (ppm)
4-12	46	Personal sample: wafer etching operator, Area 2, HF filter	9:11 11:58	11:03 14:15	486	5.4	0.01 (0.01)	
4-12	47	Wafer etching area: between booths, Area 2, HF filter	8:58	14:20	670	2.9	<0.01 (<0.01)	
4-12	48	Wafer etching area: beside Sample 47, Area 2, HF bubbler	9:03	11:02	119	<1.5	<0.01 (<0.02)	
4-12	49	Wafer etching area: beside Sample 45, Area 1, HF bubbler	8:52	9:52	60	4.4	0.07 (0.11)	
4-12	57	Wafer etching area: between booths, Area 2, HF bubbler	11:06	14:16	190	2.4	0.01 (0.02)	
4-12	58	Wafer etching area: midroom, Area 1, HF bubbler	9:59	14:10	251	2.0	0.01 (0.01)	

TABLE B-7. SAMPLING SUMMARY SHEET: PHOTOVOLTAIC PLANT SURVEY

PLANT: B

Sampling for NO_x

Process or area:
Wafer etching

Date 1979	Sample No.	Sample description		Time		Sample volume, liters	Total weight, mg	Concentration	
				Start	Stop			mg/m^3 (ppm)	Estimated TWA, mg/m^3 (ppm)
	15	Wafer etching area sample: midroom	NO	13:44	15:44	7.9	1.3	0.16 (0.13)	
			NO_2				1.2	0.15 (0.09)	
	26	Personal sample: wafer etching operator	NO	9:02	15:53	27.9	2.7	0.10 (0.08)	
			NO_2				2.4	0.09 (0.05)	
	51	Personal sample: wafer etching operator	NO	9:13	14:19	20.4	3.5	0.17 (0.14)	
			NO_2				2.3	0.11 (0.06)	
	52	Wafer etching area sample: midroom	NO	9:19	14:19	19.6	2.0	0.10 (0.08)	
			NO_2				2.0	0.10 (0.05)	

TABLE B-8. SAMPLING SUMMARY SHEET: PHOTOVOLTAIC PLANT SURVEY

PLANT: B

Sampling for solvent

Process or area:
Wafer cleaning

Date 1979	Sample No.	Sample description		Time		Sample volume, liters	Total weight, mg	Concentration	
				Start	Stop			mg/m^3 (ppm)	Estimated TWA, mg/m^3 (ppm)
4-10	7	Personal sample: wafer cleaning operator	TCF	9:30	15:40	57.9	18.1	312 (41)	
			IPA				1.3	22 (9)	

TABLE B-9. SAMPLING SUMMARY SHEET: PHOTOVOLTAIC PLANT SURVEY

PLANT: B

Sampling for arsenic

Process or area:
GaAs process

Date 1979	Sample No.	Sample description	Time		Sample volume, liters	Total weight, mg	Concentration	
			Start	Stop			µg/m³	
4-10	9	GaAs wafer slicing: personal sample	8:42	15:34	824	12.3	14.9	
4-10	10	GaAs wafer slicing: area sample near operator in Sample 9	8:40	15:34	849	12.7	15.0	
4-11	28	GaAs wafer slicing: personal sample	8:17	16:10	1135	12.8	11.3	
4-11	29	GaAs wafer slicing: area sample near operator in Sample 28	8:18	16:09	942	12.3	13.1	
4-11	34	Breakout of GaAs quartz cylinder	10:43	10:50	13	<0.05	<3.8	
4-12	55	GaAs preparation area: personal sample	10:34	11:05	63	5.50	87.3	

TABLE B-10. SAMPLING SUMMARY SHEET: PHOTOVOLTAIC PLANT SURVEY

Plant: B

Wipe samples for arsenic

Processor area:
GaAs production

Date 1979	Sample No.	Sample description	Total weight, μg	Surface concentration, mg/m^2
4-12	66	Ingot slicing: cabinet top	315	3.39
4-12	68	GaAs crucible assembly, as weighing: top of system	120	1.29
4-12	69	As weighing: hood top	1210	13.0
4-12	70	Crucible welding operation: tabletop	1230	13.3

TABLE B-11. SAMPLING SUMMARY

Location or job title	Pollutant	No. of TWA determinations	Range	Mean	No. of short-term samples	Short-term peak
Siemen process	Partic.	3	<0.02-0.11 mg/m^3	0.05 mg/m^3	1	0.07 mg/m^3
Cz ingot growing	Partic.	4	0.13-0.26 mg/m^3	0.20 mg/m^3	2	0.19 mg/m^3
Ingot cropping	Partic.	2	0.24-0.34 mg/m^3	0.29 mg/m^3	0	
Ingot grinding	Partic.	2	0.22-0.24 mg/m^3	0.23 mg/m^3	0	
Ingot etching	HF	3	0.56-0.86 mg/m^3 (0.81-1.25 ppm)	0.68 mg/m^3 (0.99 ppm)	1	3.45 mg/m^3
Wafer slicing	Partic.	3	0.34-0.52 mg/m^3	0.41 mg/m^3	0	
Wafer etching	HF	7	0.01-0.60 mg/m^3 (0.01-0.87 ppm)	0.13 mg/m^3 (0.19 ppm)	3	0.07 mg/m^3 (0.11 ppm)
	NO_2	3	0.09-0.11 mg/m^3 (0.05-0.06 ppm)	0.10 mg/m^3 (0.05 ppm)	1	0.15 mg/m^3 (0.09 ppm)
Wafer cleaning	TCF	1	312 mg/m^3 (41 ppm)		0	
	IPA	1	22 mg/m^3 (9 ppm)		0	
GaAs wafer slicing	As	4	11.3-15.0 μg/m^3	13.6 μg/m^3	0	
GaAs preparation	As	0			2	87.3 μg/m^3

TABLE B-12. WAFER ETCHING HOOD FACE VELOCITY MEASUREMENT SUMMARY

Hood No.	Cross-Section Face Velocity--ft/min						Average
	Top			Bottom			
	Left	center	Right	Left	center	Right	
101	160	170	200	200	220	120	178
102	220	350	50	240	300	230	228
103	170	200	240	250	250	240	225
104	180	240	240	190	100	230	197
105	250	300	150	230	280	230	240
106	200	180	200	260	270	230	230
107	290	290	360	350	390	380	350

Ingot Cropping and Rounding

Table B-3 summarizes personal particulate air sampling conducted in the ingot cropping and rounding work areas. Replicated samples collected in both areas showed very low exposures. Each personal sample was for essentially the full-shift exposure. In the ingot cropping area, the operator exposures were 0.24 and 0.34 mg/m^3; for the ingot rounding, the exposures were 0.24 and 0.22 mg/m^3. For three of the samples, total SiO_2 and crystalline quartz analyses were run. The levels were very low in each case, with the crystalline quartz fraction being below the detectable limit in each sample.

The ventilation on the ingot cropping saws was insufficient in all cases for good capture. Further, the guard on two of the saws had been cut off.

Particulate emissions were generally well controlled in both of these work areas. No significant health-related problems were found.

Ingot Etching

Table B-4 presents results of personal and area samples collected in the ingot etching area for HF exposure. All samples were collected on impregnated filters. Only one sample exceeded the current TLV of 2 mg/m^3 (or 3 ppm) for HF with a concentration of 3.45 mg/m^3 (5.0 ppm). This was a 1-1/2-hour area sample collected just above one of the ingot etching assemblies. The position is likely to be one of high concentration because emissions occur primarily between etching cycles when the assembly lid is opened. All other samples showed exposures of less than half of the TLV.

The ingot etching ventilation face velocities measured with the lid open were 13 to 16 m/min (40 to 50 ft/min). As a result, this assembly appears adequate only if the lid is kept closed and no nitrogen oxides are present. When the lid is opened, acid fumes were observed to be released. Additional control is recommended during this operating mode.

Operators wore appropriate safety protection during operation to avoid accidental contact with HF.

Wafer Slicing

Table B-5 presents particulate sampling results for the wafer slicing area. The personal samples showed 0.34 and 0.52 mg/m^3 exposure. An area sample collected in the work area of the latter personal sample resulted in 0.36 mg/m^3 concentration.

Both personal samples were analyzed for total silica and crystalline quartz. The crystalline quartz level was below the detectable level in both samples; the total silica was below the detectable level in one sample and less than 25 percent of the sample in the other. No significant health problems were found in this area.

Wafer Etching

The wafer etching work areas were sampled for airborne HF and nitrogen oxides (specifically NO and NO_2). The results are summarized in Tables B-6 and B-7. Samples were taken from etching area No. 1 unless specifically noted as from area No. 2. Only two HF samples showed elevated levels, at 0.87 and 0.51 ppm; nearly all other results were less than 0.05 ppm. No specific reason is known for these two elevated levels. The HF thus appears to be satisfactorily controlled. Both HF bubbler and impregnated filter samples were collected in this work area. In cases in which matching samples were collected for use in comparing the two sampling media, the concentrations were too low for an adequate comparison.

The sample results for nitrogen oxides are presented in Table B-7. The results of two personal and two area samples were all less than 0.15 ppm of NO and less than 0.10 ppm of NO_2. Their respective TLV's are 25 ppm and 5 ppm. Thus nitrogen oxides also appear adequately controlled.

Protective coats, smocks, and face shields were worn at all times during operation. This program appeared quite effective.

Table B-12 summarizes hood face velocity measurements taken for each etching hood. Face velocities were generally adequate, a fact that is reflected by the low HF and NO_x concentrations found in the work environment. In area No. 1 (for hoods 101, 102, 103, 104, 105), the face velocities had variations as high as ±0.25 to 0.51 m/s (±50 to 100 ft/min) because of the turbulence caused by poor supply air diffusion and location over the hoods. Better control could be achieved with less air by better diffusion of supply air diffusion. In area No. 2 the supply air was back away from the hoods and less turbulence was found at the hoods.

Wafer Cleaning

After ingot slicing, the wafers are cleaned in a series of solutions to remove surface impurities prior to etching. Table B-8 presents the results of a personal sample analyzed for solvent exposure, specifically to trichlorotrifluoroethane and isopropanol. The TWA operator exposure level was 44 ppm of TCF and 22 ppm of IPA. Both concentrations are well below the TLV.

Two wafer cleaning lines were used, each with 11 tanks of solutions in which the wafers in baskets are automatically immersed sequentially. The first 9 tanks contain a soap solution; the last two contain IPA and then TCE. These two hoods have slots at the ends of the tanks to control emissions. One cleaning line appeared well balanced. The slot velocities were 1900 to 2500 ft/min and tank face velocities were 13 to 30 m/min (40 to 100 ft/min). This system appeared adequate. The second system, near the room entrance, had 305 m/min (1000 ft/min) slot velocity and tank surface velocities of 2 to 6 m/min (5 to 20 ft/min). This system appeared poorly balanced, in part because of air supply interference. Capture velocity was too low. Improved local ventilation on Unit 2 would be likely to substantially reduce operator exposure to solvents.

GaAs Production

Tables B-9 and B-10 summarize samples collected in the GaAs production area to monitor for arsenic. Full-shift samples collected in the GaAs wafer slicing area showed consistent exposure levels (Table B-9). One operator was exposed to 14.9 $\mu g/m^3$ of arsenic; an area sample collected in a central room area was 15.0 $\mu g/m^3$. The second personal sample showed 11.3 $\mu g/m^3$ arsenic exposure; the area sample was 13.1 $\mu g/m^3$. Other samples were collected to monitor intermittent operations. A personal sample collected during breakout of GaAs quartz cylinders was below the detectable level, but the short duration of the sample limits the usefulness of this result. Another personal sample was collected during preparation of GaAs cylinders. The exposure was 87.3 $\mu g/m^3$ of arsenic for a 31-minute sample. This level may be substantially above the federal standard of 10 $\mu g/m^3$ TWA (179). Full-shift samples in the preparation area would be useful in assessing overall exposure.

Table B-10 presents the results of wipe samples collected in the GaAs process areas. Samples were collected by wiping equipment surfaces with Watman filter paper. In each sample, a surface of 0.3 m^2 (1 ft^2) was wiped and the results were reported as milligrams of arsenic per square meter of surface. Four samples showed a buildup of from 1.3 to 13.3 mg/m^2. Although there is no standard to apply to these results, and no standard procedure for collecting such samples, the results do indicate the relative cleanliness of the work areas. Workers can contaminate clothing inadvertently, the material can be ingested, or it can be reentrained. In work areas having the higher arsenic buildup, the arsenic weighing hood top and the crucible welding tabletop should probably be cleaned more often.

CONCLUSIONS

A significant industrial hygiene problem was found as over-exposure to arsenic, which exceeded the federal standard. Personal exposures were uniformly well below applicable standards, with the exception of arsenic exposure.

Ventilation control and enclosure of operations during which gallium and arsenide is prepared for GaAs production and during the slicing of wafers should be improved. It is recommended that periodic wipe samples be collected in the above areas to monitor cleanup practices and help determine overall control efficiency.

It should be stressed that the method for analyzing arsenic is not specific for free elemental arsenic but will report arsenic in combination with other elements. Therefore, arsenic detected in the samples collected may be present in combination with gallium.

PLANT C: SILICON WAFER PRODUCTION FACILITY
WALK-THROUGH SURVEY

PLANT DECRIPTION

Plant C consists of several buildings of interest for production of photovoltaic materials. The plant produces only polycrystalline silicon for the electronics and photovoltaics industry. Less than 1 percent of plant production is estimated to be used in photovoltaic applications.

The plant is described in this report in the order in which the walk-through was conducted.

Incoming Materials

Liquid hydrogen is stored in tanks for supply to the production facilities, and the maintenance and safety of that storage area are the responsibility of the supplier.

No hydrogen monitors are in use. At any point where hydrogen enters a building, a high air flow is reportedly used to lessen the likelihood of formation of an explosive atmosphere. All production buildings in which hazardous materials are used reportedly undergo an air change every 13 or 16 seconds, depending upon the operational mode of the ventilation equipment.

Trichlorosilane (TCS) is brought to the site in tank trucks and is transferred into tanks under nitrogen pressure of approximately 0.5 to 3.7 atm (7 to 55 psi). All bulk unloading operations are described in written safety procedures. In any operation where a connection is broken, full chemical goggles are required. Excess TCS is scrubbed from the nitrogen pressurization gas in a scrubber. Total material balance for TCS is reportedly much less than 1 percent loss.

Feed System

Hydrogen and TCS are combined in a mixer, which is never opened except for maintenance. This mixer is purged with nitrogen before maintenance personnel open it, no TCS odors are reportedly encountered. The TCS reacts rapidly with moist air to form hydrogen chloride and is therefore reportedly easily sensed.

Decomposition Reactors

Reactor rooms contain several Siemens process decomposition reactors, in which the hydrogen and TCS are reacted at approximately 1100°C to form polycrystalline silicon. In the center of the reactor used, a U-shaped seed rod of single-crystal silicon serves as an electrically heated filament, on the surface of which the silicon from the decomposed TCS deposits. The reactor rooms reportedly undergo an air change every 13 seconds, so that a concentration of hydrogen from a leak is unlikely to reach a significant fraction of the lower explosive limit. The reactors run for tens to hundreds of hours, depending on the size of polysilicon rod desired. "Turning around" a reactor for further use is the most likely means of exposure to unreacted TCS, silicon tetrachloride, and hydrogen chloride byproducts. Six people normally work in and around the reactor room.

White powder was noticed on the walls and rafters and on the outside of a cracked reactor. This material was reported to be polysiloxanes and possibly amorphous silica. A rafter sample was taken in the reactor room and from the encrusted material on the cracked reactor. Both samples were analyzed by X-ray diffraction for crystalline silica, and none was found (limit of detection is 1%).

The byproducts of the decomposition reaction are reported to be hydrogen, unreacted silanes, silicon tetrachloride, and hydrogen chloride. All byproducts are recovered and reused or sold.

Rough Rod Cutting, Drilling, and Grinding

Purity samples are taken with a core drill, cutting under water, for visual inspection of the inside of the rod. Rods are cut in two in this area with a water-drenched diamond-tipped saw. During cutting, silicon slurry is thrown onto the walls of the room and is considered to be a nuisance dust. Wastewater from the saws goes through a sand filter.

Silicon Tetrachloride Trailers

Silicon tetrachloride is put into tank trailers for shipment. In this and all other tanker operations, filling and emptying operations are done for both the liquid and vapor phases.

Crucible Charge Cutting Area

In the crucible charge cutting area, polycrystalline rods are cut to the precise weight ordered by the customer. These rods are used in crucible charging for Czochralski crystal pulling (not done at Plant C). The rods are cut on handsaws. Other rods are centerless ground for float zone processing by customers. Sawing and grinding are done wet, with a coolant composed of water and a lubricant.

Silicon Cleaning Room

The cut pieces of silicon are surface-etched and cleaned before shipment to the customer. The chemicals used in cleaning the silicon are trichloroethane, nitric acid, hydrofluoric acid, and water. The fumes from the acid wash are exhausted through a scrubber. All employees in this area are required to wear acid-resistant gowns, gloves, and chemical goggles.

Thin Rod Production Area

The thin rod production area contains vacuum furnaces in which thin seed rods are produced from other seeds by the Czochralski crystal pulling method. The vacuum furnaces contain radio frequency (RF) induction coils. No monitoring has reportedly been done for RF energy.

SUMMARY AND CONCLUSIONS

Hydrogen System

The hydrogen system seems to be very well maintained. Because handling and maintenance of this equipment are conducted by a supplier, the potential industrial hygiene hazard to Plant C employees is minimal, and no industrial hygiene followup would be anticipated.

Unloading TCS

Tank trucks containing high-purity TCS are unloaded under nitrogen pressurization into holding tanks. Reportedly, specific written procedures are followed, and safety equipment (goggles, clothing, respirators) is used. The white "fogging" on nearby painted surfaces indicates possible leakage of TCS/HCl during unloading. Air sampling would be appropriate to verify the levels. In general, safety procedures seem adequate, but industrial hygiene followup would be appropriate.

Mixing Hydrogen and TCS

Hydrogen is mixed with TCS just outside the production building, with the resulting mixture piped into the reactor rooms. Purging procedures as reported seem adequate to minimize hazard potential. No industrial hygiene followup would be anticipated.

Main Production Plant

Conditions in all reactor rooms containing the silicon rod production reactors were essentially the same. Heavy accumulations of a white powder on the ceilings indicated that process materials become airborne and remain in the air long enough to permit contact with building surfaces. The most likely occasion for contaminant release and resulting personnel exposure would be during reactor turnaround. This reportedly has been monitored on an irregular basis, with levels found to be within acceptable limits.

White "fogging" of glass, metal, and painted surfaces was observed throughout the building, including the hallway and stairway.

Ventilation in the reactor rooms was relatively elaborate. The rooms were clearly constructed with every intention of providing adequate control. During the winter months, fresh air is preheated by a heat-wheel exchanger from the exhaust air. Air is exhausted through large panels on the inside wall of the room. During the summer months, fresh air is taken in through manually operated louvers in the outside walls, with exhaust through roof ventilators. The rated volume flowrate capacities of these systems are reportedly quite high.

Accumulations of materials throughout the building, which are very substantial in the vessel rooms, indicate that contaminants are released and dispersed throughout the reactor rooms and connecting hallway. The basic concept of the ventilation system is dispersive rather than containing. Conditioned air supply from the ceilings, with local exhaust at the base and/or rear of each reactor, would seem more appropriate.

A small portable exhauster is used for localized ventilation during special operations. This unit discharged into the room at a level about 2.4 m (8 ft) above the floor. Followup evaluation of this procedure would be appropriate, because contaminants are released into the room and because the control capability of the general ventilation system has not been verified.

General safety precautions, such as emergency venting in the event of reactor overpressurization and warning alarm in the event of leakage causing pressure loss, seem adequate.

Air sampling, ventilation measurements, and industrial hygiene followup would be advisable in the reactor rooms and the connecting hallway.

Rough Rod Cutting, Drilling, and Grinding

Local controls (both exhaust ventilation and water spray) seem adequately designed. Slight silicon dust accumulations were observed on machine surfaces. These controls and the very limited personnel time that the operations require (reportedly one-half hour per day) would not suggest the need for extensive industrial hygiene followup.

Material Recovery Processes

Material recovery operations and work areas were covered rather quickly and with little detail offered, largely for security reasons. The processes are reportedly very efficient, with almost no loss except for a small amount of hydrogen at the compressors. Painted surface "fogging" was observed throughout the outside area. Reportedly no full-time personnel are in these areas.

Potential exposures would involve hydrogen, HCl, TCS, and other chlorosilanes. Reportedly, no comprehensive industrial hygiene evaluations have been conducted for these processes. Followup would seem appropriate, but more details of chemical and personnel procedures would be required.

Final Rod Cutting

Local controls, exhaust ventilation, and water spraying were used for the handsaws and other cutting machines. These controls appeared to be adequate. Little or no industrial hygiene followup would be anticipated.

Cleaning Room

All work pieces reportedly passed through a trichloroethane cleaner. No local exhaust ventilation is provided for this tank, which is reportedly covered when not in use. Air sampling would be appropriate to determine personnel levels.

Acid wash/etching operations, involving nitric and hydrofluoric acids, are carried out with local exhaust ventilation. Air sampling has reportedly been conducted at levels found to be acceptable.

A small exhaust blower with a flexible hose is used for dust control when baskets of silicon fragments are emptied into drums.

Air sampling and ventilation evaluations would be appropriate as part of an industrial hygiene followup for this area.

Thin Rod Production Area

Thin silicon rods are drawn from meltdown of larger rod fragments. Electric melting furnaces are used; this may pose a hazard from RF waves.

General

Operations at this plant are conducted with a strong awareness and concern for health and safety. Workers are trained in safety procedures, first aid, and firefighting. All persons involved with the survey were helpful, knowledgeable, and seemed committed to safety and health. The corporate industrial hygiene staff seems to be qualified and well informed. They have been closely involved with the plant operations and cooperate fully with production personnel, while retaining independent authority and responsibility.

RECOMMENDATIONS

As indicated above, the primary areas for industrial hygiene followup would be:

Unloading area for TCS tank trucks
Vessel rooms in the main production plant
Material recovery processes
Cleaning room

Operations at this facility may not be extensive enough to represent operations throughout the photovoltaic cell industry.

PLANT D: SILICON WAFER PRODUCER
WALK-THROUGH SURVEY

SUMMARY OF SURVEY FINDINGS

Process operations at Plant D encompass ingot growing to polished wafers. Many operations were necessitated by semiconductor quality control requirements that are not necessary for photovoltaic applications. Generally, few occupational problems were observed. Ingot grinding and preparation appeared to be the dirtiest operations.

PLANT DESCRIPTION

Plant D is a privately owned corporation producing polished silicon wafers, custom equipment, and ceramic packaging. The facility occupies six buildings with a total floor area of 57,000 ft^2. In 9 years of operation, production has progressively expanded.

DESCRIPTION OF WORK FORCE

Plant D employs about 300 production workers, of which about 60 percent are women. The plant operates three shifts a day with the majority of the workers on the day shift and the remainder divided evenly among the other two shifts. The age spread of production workers is roughly as follows: 40 percent are 20 to 30 years old, 30 percent are 30 to 40 years old, and 30 percent are over 40 years old. Labor turnover is fairly high; the average tenure is 2 years. Little previous training is required for most jobs, and no predominant industrial background was reported.

PRODUCTION PROCESSES

Ingot Growing

Twenty furnaces designed by Plant D are operated all in one room. The polysilicon charge is 10 kg (22 lb), with a capacity of up to 12 kg (26.5 lb). An argon protective atmosphere is maintained at a slightly positive pressure. A trend toward vacuum operation was reported, also in an argon atmosphere. This would, however, reduce the oxide building up outside the crucibles. At the end of a growing cycle, the crucible is cooled 1-1/2 hours, and the assembly is vacuum-cleaned and wiped with isopropyl/alcohol. In case of power failure, the charge is lost; a water failure can ruin the base plate. According to reports, however, such failures seldom occur.

Plant D is currently working on a continuously replenished melt system, which would lower cost considerably. Crucibles could last about a week instead of being discarded after each ingot. Also, less silicon would be wasted.

Some ingots are n-doped with phosphorus, some are p-doped with boron, and a few are doped with magnesium. The semiconductor industry is by far the major user. The furnaces are operated continuously and require six operators.

Ingot Preparation and Slicing

Both ends of each ingot are cut or cropped off by specially designed, rotating, diamond-blade cutters. Three separate units are used. An enclosed sand blast unit removes any oxide layer from the ingot.

Ingots are cylindrically ground round to a specified diameter by one of four grinders. The grinders use a diamond blade and water rinse.

The crystal reference plane is located on film, and a flat surface is ground on the ingot for future alignment reference by the wafer customer.

The prepared ingot is etched and rinsed to remove any work damage. The dried ingot is then mounted with an epoxy adhesive.

The ingots are vertically mounted and sliced by single-blade diamond saws. A total of 28 units are used, each with water jet lubrication. The slicing is completely automated, requiring only six operators. The kerf loss is carried away by the lubrication water and drains to a common reservoir outside.

Wafer Etching

After being sawn, wafers are placed in boats, etched by a concentrated solution of hydrofluoric-acetic acid and nitric acid, and rinsed with water to clean them and remove work damage. The boat is loaded onto a mechanical arm, and the front sliding door to the hooded system is then closed, thus isolating this operation.

In an automatically timed operation, the boat is submerged in the acid, submerged in the water rinse, and then taken out. Two etching units are operated by two workers in a separate room. The etched wafers are rinsed and dried in a centrifuge.

Wafer Polishing

Wafers are polished by a mechanical polishing process designed by Plant D to remove work damage. Wafers are mounted in a circular pattern on flat circular vinyl polish carriers. The mounted wafers on the polish carriers are placed in enclosed centrifuges to control temperature and pressure. Ludox, a polishing slurry containing colloidal silicon, is injected between the wafer and a rotating pad. This operation requires about 30 minutes and is performed 24 hours a day, 5 days a week. Some polishing slurry is recirculated, and the remainder is dumped.

Mounting and removing wafers from polish carriers are labor intensive, requiring five operators.

Final Cleaning and Packaging

Wafers in boats pass to a clean room, isolated from the rest of the building. Some wafers go through a second polishing sequence, including dips in triton-X, ammonium hydroxide, and water and drying. Two cleaning tracks are used, each with a sequence of baths. The sequence is: (1) water, (2) dilute hydrofluoric acid (HF), (3) water, (4) sometimes acetone, (5) trichlorethylene, and (6) hydrogen peroxide and ammonium hydroxide. Wafers are then dried by spinning and packaged. This is also a labor intensive sequence of operations.

SURVEY OBSERVATIONS

Ingot Growing

Although the production scale is relatively large, the ingot growing room was clean. General ventilation was used.

Ingot Preparation and Slicing

Ingot preparation and slicing accounted for the dirtiest work environment in the plant, primarily because of particulate matter (kerf loss) from ingot cutting. The ingot cropping machines were the noisiest, but did not appear to present an occupational problem. Ingot grinding (for uniform diameter) was the dirtiest operation. The four grinders were shielded, and two of them were provided with ventilation ducting. All equipment was heavily coated with particulate matter. Two machines that were specially designed to cut a flat reference plane on the ingot produced little visible airborne particulate matter. An operator on one of the cutters had a severe skin rash on his hands, which were quite dirty from handling ingots. Operators wore no protective equipment and were generally quite dirty in this area. Wafer slicing was automated and quite clean.

Wafer Etching

Wafer etching with concentrated HF, acetic, and nitric acids is automatically controlled, so that only two operators load and unload. The baths are in a closed ventilated hood. Each operator wore protective cap, gown, and gloves.

In case of a power loss, emergency lights are available, and the acid bath automatically drains. No alarm, however, is provided for loss of hood ventilation. The bath stood in a shallow retaining wall that appeared sufficient to contain spills and leaks effectively. Waste acid is drained to a separate neutralizing basin before disposal. Generally this operation appeared well controlled.

Wafer Polishing

Wafer polishing operations appeared to be of little industrial hygiene concern. The polishing slurry was well contained with little operator contact.

Final Polishing and Packaging

Final polishing and packaging were conducted in a clean room with wet operations in laminar flow hoods. Operators wore full protective clothing. Although these control measures are needed for quality control, the effect is a well controlled environment for workers.

COMMENTS

Most operations appeared well controlled. Some workers in the wafer slicing area were quite dirty. Thus protective clothing would be helpful together with added attention to personal hygiene. The observed case of severe skin rash may be job-related.

Air sampling or ventilation measurements would be appropriate in several areas. Particulate matter should be measured near the four grinders that grind the ingots round and near the grinders producing a flat reference plane on the ingots. Ventilation on the etching hoods where HF-acetic and nitric acids are used should be tested, as should the adequacy of fail-safe systems on these operations. Finally, particulate matter should be measured in the wafer polishing area, and ventilation should be tested in the final wafer cleaning operations.

PLANT E: SILICON MODULE PROCEDURE IN-DEPTH SURVEY

INTRODUCTION

A walk-through survey was conducted at Plant E on November 2, 1978. Plant E was chosen for an in-depth survey because it is a relatively new facility using what is believed to be mostly state-of-the-art technology.

SUMMARY OF SURVEY FINDINGS

Plant E produces silicon solar panels, starting either with ingot growing or purchased wafers. Most production operations are conducted in two large open rooms. This is a new and expanding facility. No serious industrial hygiene problems were observed.

PLANT DESCRIPTION

Plant E began operation in October 1977 and moved to the present facility in March 1978. The facility is housed in one building and has been progressively expanding. It produces solar cells and panels plus accessory equipment, such as pole mounts.

DESCRIPTION OF WORK FORCE

Currently, less than 100 people are on the payroll, of whom about 65 percent are in the production area. They operate 5 days a week on the day shift and part of the second shift. Most production personnel are young, averaging 21 to 22 years of age; about half are women. The employment application includes a work history of the previous 2 to 3 years.

All employees are given a physical examination when they are hired and at regular intervals thereafter. No characteristic lost-time accident trends have been observed.

PRODUCTION PROCESSES

Ingot Growing and Slicing

A separate room houses 2 Czochralski crystal growers. Although the growers were operating, most wafers were purchased. The Czochralski process will be used at least for the next 3 to 5 years to make the plant self-sufficient in wafer production.

The growers maintain a jacket of circulating cooling water with an alarm system and a hookup to city water that can be manually actuated.

One grower was observed between cycles. The inside walls were uniformly coated with a very fine dust layer about 5 mm thick. This is removed after every cycle by first using a portable vacuum cleaner and finally wiping all surfaces with cloth soaked in a Freon compound. The dust, silicon oxide, comes from oxygen leaks through the crucible. The vapor space around the crucible is under slight positive pressure from nitrogen. Newer units maintain a vacuum in the space, reportedly minimizing this oxide buildup.

One or two workers were located in this area.

Three single-blade diamond saws were used to cut wafers from ingots. Ingots are sent out to be ground round prior to mounting and sawing. These saws had only been in operation one month. The saws are highly automated, requiring only operator mounting.

The saws are equipped with water lubrication to the saw blades. The water flows with kerf loss to a small reservoir. Clarifed water is drawn off while the sludge is dried and disposed. Only a part-time operator appeared to be in this area.

Wafer Cleaning, Rinsing, and Etching

After sawing, wafers in boats are cleaned in sequential baths of dilute potassium hydroxide and deionized water. The wafers are rinsed and dried by air in a centrifuge. Wafers, still in boats, are then etched and rinsed in a series of vats. A caustic solution and then a weak caustic solution is used; three cascade rinses follow.

Following the tube furnace diffusion, the wafers passed through a series of baths: first dilute cold sulfuric acid and hydrogen peroxide, then three water rinses. The wafers were transferred to a centrifuge where they were rinsed and dried by air at elevated temperature.

The wafers, in boats, were transferred manually between operations. Each series of cleaning or etching operations was done in connected baths. About 4 to 5 workers were in this area.

Diffusion Junction Formation

A tube furnace is used to diffuse the phosphorus n-doped layer on the wafers with phosphorus oxychloride ($POCl_3$). The diffusion cycle is automatically controlled, requiring an operator only to insert the rack of wafers and to remove them after the cycle. The cycle, which takes 1/2 to 1-1/2 hours, consists of preheat, doping material deposition, and bake. After removal from the furnace, the wafers cool and are transferred to boats for etching. Only one part-time operator was in this area.

Apply Contacts

Contacts are applied with the screen printing method. A silver paste is printed automatically on wafers as a thin grid. An operator loads wafers to the paste applicator, from which they move two at a time on a conveyor through a low-temperature dryer and through an ultraviolet (UV) belt furnace to fire the contacts. The wafers pass through this operation twice. First a back screen is applied, and then a front screen is applied.

The wafers are cooled and etched with a low-concentration HF.

Before wafer preparation of assembly, the wafers pass through a plasma edger and are electrically tested. The plasma edger, which prepares the cell edges for array assembly, is performed in a manually loaded vessel. The operating sequence consists of preheat, pulling a vacuum, operating in a Freon-14 atmosphere, and breaking the vacuum.

Cell Assembly

Cell assembly into panels is performed in a separate room and is generally much more labor intensive than the preceding cell preparation steps. Polyvinyl butyrate (PVB) sheets that have been cut with a die are used as the pattern for cells to be mounted and soldered in place. After inserting cells in the sheets, the operator applies a silver-tin solder paste to contact locations and sets the contact with a solder gun. The amount of paste delivered is automatically controlled. After inspection, the arrays are cleaned with a cloth soaked in solvent containing isopropyl alcohol and Freon. About six operators were involved in this area.

The cells in the PVB sheets are laminated on a precut glass sheet with a tedlar backing. The rolled tedlar is kept in an enclosed, vented assembly, in which the sheet is given a high-voltage contact before removal to impart better adherence characteristics. The glass, PVB (with cells), and tedlar are mounted and taped onto a palate. A vacuum is applied to the edges, and a flat hot plate is applied to the palate assembly. This operation required about four operators.

The final operations after removing the assembly from the palate and cooling were to trim the edges, cut holes in the sheet for terminal screws, and put in the final case. The screws were sealed with polysulfide. The final modules were cleaned with a razor blade, wiped with isopropyl alcohol, and electrically tested. These operations required about five operators.

Silicon crystals were grown in a relatively small room. Two machines were used. The operation involved a low purge flow of argon gas to minimize oxidation within the growing chamber. The crystal growing chambers were not evacuated, and there was no local exhaust ventilation on these machines.

The argon purge was discharged through an oil bubbler. Some amorphous silicon oxide may be removed by the purge flow, and most would be collected in the bubbler. This part of the process appeared to pose no health hazard.

Amorphous silicon oxide was deposited on the inside surface of the chamber during crystal growing. These surfaces must be cleaned between production runs for each crystal. Local exhaust ventilation in the form of a portable "shop" vacuum cleaner was used for primary cleaning. Final cleaning was achieved by hand-washdown with Freon TF and limited blowoff with compressed air.

Silicon and silicon oxide coating appeared to consist of very fine particles. When displaced from the chamber surfaces, the coating tended to fall in relatively large "flakes." No fine airborne dust was observed during cleaning operations; nor were significant accumulations noted within the room.

Observed cleaning procedures were very thorough, as necessary for process purposes. Vacuum cleaning appeared effective and non-dispersive. Reports state, however, that airborne "dustiness" sometimes results from rushing the cleaning process or cleaning both machines at one time.

General ventilation for the crystal growing room consisted of two air supply registers and one exhaust grill, all located on the ceiling. The primary purpose of the ventilation was cooling of the room. Although this was accomplished, the proximity of supply and exhaust openings may have resulted in some "short-circuiting" of the ventilation air flow.

The general ventilation system recirculated air to an evaporative cooling unit for resupply. The system reportedly operated at about 100 percent recirculation. The system maintains a steady pressure in the growing room. The pressure was neutral with respect to nearby plant areas, with essentially still air at the doorway. Some air mixing and dilution would be expected with the introduction of return air from an adjacent laboratory area, which was serviced by the same air handling system. General ventilation was considered adequate.

Cleaning, Rinsing, and Etching of Wafers

All wet chemistry operations were conducted in cascading bath assemblies. Downflow ventilation slots were on the back three sides of each bath. No hooding assemblies were used.

The baths and operator locations or "wet-lines" were mounted on wooden slats for easy draining into wastewater channels below. The wet-lines were rinsed daily. Operators wore protective coats and gloves. Wastewater flowed to neutralizing tanks in the floor before disposal. Acids were delivered daily and kept under the hoods; caustic was kept as a solid. An emergency shower and eye-wash were located in this area.

No added area ventilation was provided, and no health problems were evident. The wet-lines probably should be in a separate room and covered with hooding in case of power failure.

Diffusion Junction Formation

Diffusion junction formation appeared to be a clean operation. The loading end of the tube furnace was connected to a side ventilation duct. The $POCl_3$ was kept in quartz bubblers, which last 4 to 6 months. The connection nipples on new quartz bubblers are sealed and are only broken as the valves are connected. This appeared to be a simple and safe assembly. Nitrogen and oxygen gas cylinders were chained to an adjacent wall. The gas ducting might be simplified. Precautions need to be taken to prevent release of $POCl_3$, possibly with an alarm and automatic shutoff assembly and proper ventilization and isolation of this area.

Application of Contacts

The operation to apply contacts was quite automated and appeared to present few worker exposure concerns. The operator loading the cells supplied the silver paste to the dispenser. She wore a glove on one hand. Attention should be given to her personal hygiene. The belt furnace was connected to a natural-draft vent. No visual emissions were evident. Solids are collected separately in this work area to try to reclaim silver.

Cell Assembly

Although no local ventilation was provided for the soldering operations, solder usage is low, and a very low fume generation rate was observed. The arrays were cleaned with isopropyl alcohol by workers with bare hands.

The tedlar dispenser appeared well enclosed and vented to avoid exposure to the high-voltage sources.

A canopy hood covered the hot plate operation used to bake the array laminated sheets. Operators, however, worked under the hood and could be exposed to some plastic monomer or degradation products.

The final assembly operations are simple labor intensive operations of little industrial hygiene concern.

SURVEY PROCEDURES

Air samples were collected to evaluate worker exposures to particulates and silica in the ingot growing and slicing areas. Also, during cleaning of the ingot growers, solvent exposures were monitored. Samples were collected and analyzed for silver in the metallization process. In the cell interconnection area, samples were collected and analyzed for lead. Particulate samples were collected in the module lamination area, and samples were collected for solvent exposure in the module cleaning step. The solvents used contained trichlorotrifluorethane (TCF) and 1,1,1-trichloroethane (TCE).

Summarized below are brief descriptions of the techniques used to collect and analyze the air samples obtained during the survey.

Particulate Samples

All particulate air samples, both personal and area, were obtained by drawing air at a flow rate of about 2 liters (0.8 gal) per minute through standard closed-face PVC filter cassettes; Mine Safety Appliances Model G or Bendix closed-face BDX 55HD personal sampling pumps were used. For personal samples, pumps were attached to the worker's belt, and the sampling tubes were clipped in a vertical position to his lapel or shirt collar. Some filter cassettes were changed halfway through the shift;

others, particularly for area samples, were used for the full shift. Some short-term peak exposure samples were collected, particularly for cleanup operations.

Selected particulate samples were also analysed for total silica (SiO_2) and crystalline α-quartz. Total SiO_2 was determined colorimetrically using NIOSH Method P&CAM 106, whereas the crystalline α-quartz fractions were determined by X-ray diffraction with NIOSH Method P&CAM 109.

Silver

Personal samples were collected from operators on the metallization pattern application for silver exposure. Samples were collected using AA filter cassettes by a method similar to that presented under particulate samples above.

In the PEDCo Environmental laboratory, samples were analyzed using NIOSH Analytical Method P&CAM 173 for silver. In this procedure, the sample containing filters are wet-ashed with nitric acid to destroy the organic matrix. The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer. A hollow cathode lamp for cadmium is used to provide a characteristic cadmium line at 328.1 nm. The absorbance is proportional to the silver concentration (1).

Lead

Personal exposure to airborne lead was monitored in the cell interconnection area. Lead was sampled by a method similar to that described for silver above.

Lead samples were analyzed in the laboratory using NIOSH Analytical Method S341(1). Samples were wet-ashed with nitric acid to destroy the organic matrix, and the lead is then solubilized in nitric acid. The solutions of samples and standards are analyzed by aspiration into the oxidizing air-acetylene flame or an atomic absorption spectrophotometer with a hollow cathode lamp for lead.

Solvent Cleaning

Samples were collected in solvent cleaning operations, specifically during cleaning of the crystal grower and cleaning of finished modules. The solvents contained TCF and TCE. Personal air samples were collected by drawing air at about 100 cc per minute through standard charcoal tubes with SKC brand low-volume pumps. The pumps were attached to the worker's belts and the sampling tubes in holders were clipped in a vertical position to his lapel or shirt collar. Collected samples were capped and kept in a freezer upon return to the laboratory.

In the laboratory, samples were analyzed using NIOSH Analytical Method S328 for TCE and TCF. In this procedure, the charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide. An aliquot of the desorbed sample is injected into a gas chromatograph. The area of the resulting peak is determined and compared with the areas obtained from the injection of standards.

RESULTS AND DISCUSSION

The results of personal and stationary air samples obtained during the survey are discussed below. Tables A-1 to E-5 present the results of sampling for particulates from ingot growing and slicing, for silver from metallization silver paste application, for lead from cell interconnection soldering, for particulates from module lamination, and for TCF and TCE from solvent cleaning, respectively. For cases in which samples were changed on a worker during the shift, the time-weighted-average (TWA) exposure is calculated. Table E-6 presents a summary of sampling results.

Ingot Growing and Slicing

Table E-1 presents the results for particulate samples collected in the ingot growing and slicing areas. Particulate exposure based on personal samples was very low in the ingot growing areas. During normal operation, full-shift exposures were 0.15 and 0.13 mg/m^3. During cleaning of the growers, particulate exposures were in the same range as during normal operation; the highest personal exposure was 0.15 mg/m^3 for a 1-1/2-hour cleaning cycle. Area samples collected during two cleaning cycles showed concentrations of 0.16 and 0.14 mg/m^3. Personal samples collected for respirable particulates were below the detectable range.

Wafer slicing operators were exposed to somewhat higher particulate levels. Personal samples collected during normal operation resulted in exposures of 0.74 and 0.44 mg/m^3.

Selected samples were also analyzed for total SiO_2 and free crystalline silica. For each of the four silica analyses, the free crystalline silica concentration was below the detectable limit. Each analysis showed less than one-third total silica by weight in the sample. The analysis of a bulk sample taken from inside the ingot grower during cleaning revealed the total SiO_2 concentration of particulates to be 16 percent and the crystalline SiO_2 concentration to be less than 1 percent.

No health or safety problems were found in this plant area.

TABLE E-1. SAMPLING SUMMARY FOR PARTICULATES FROM INGOT GROWING AND SLICING AT PLANT E

Date in 1979, month/day	Sample No.	Sample description	Time		Sample volume, liters	Total sample weight, μg	Concentration	
			Start	Stop			mg/m^3	Estimated TWA, mg/m^3
4/3/79	1	Ingot growing operator; normal operation	0953	1622	820	0.12	0.15	
4/3/79	2	Wafer slicing operator; very little operation	0951	1205	308	0.02	0.06	
4/3/79	8	Wafer slicing operator; normal operation	1327	1632	403	0.30	0.74	0.45
		Total SiO_2 Crystalline α-quartz				0.09 <0.01	0.22 <0.03	
4/3/79	10	Ingot growing operator; cleaning grower	1742	1909	200	0.03	0.15	
4/3/79	9	Same operator as at Sample 10; respirable particulates	1742	1909	149	<0.01	<0.07	
4/3/79	11	Area sample near crystal grower during cleaning	1744	1910	189	0.03	0.16	
4/4/79	13	Ingot growing operator; normal operation	0850	1625	1609	0.14	0.13	
		Total SiO_2 Crystalline α-quartz				0.04 <0.01	0.04 <0.01	

TABLE E-1 (continued)

Date in 1979, month/day	Sample No.	Sample description	Time		Sample volume, liters	Total sample weight, μg	Concentration	
			Start	Stop			mg/m^3	Estimated TWA, mg/m^3
4/4/79	14	Wafer slicing operator; light operation	0852	1202	371	0.04	0.11	
4/4/79	20	Wafer slicing operator; normal operation	1204	1634	594	0.26	0.44	0.31
		Total SiO_2 Crystalline α-quartz				0.06 <0.01	0.10 <0.02	
4/5/79	28	Ingot growing operator during cleaning; sample worn half of time	0040	0200	163	<0.01	<0.06	
4/5/79	26	Same operator as at Sample 28; respirable particulates	0041	0200	151	<0.01	<0.07	
4/5/79	27	Area sample near ingot grower during cleaning	0040	0202	147	0.02	0.14	
4/5/79	30	Grab samples of particulate coating in ingot grower walls		0100				
		Total SiO_2 Crystalline α-quartz					[a] [b]	

[a] Concentration equivalent to 16 percent of sample

[b] Concentration equivalent to <1 percent of sample.

TABLE E-2. SAMPLING SUMMARY FOR SILVER FROM METALLIZATION SILVER PASTE APPLICATION AT PLANT E

Date in 1979, month/day	Sample No.	Sample description	Time		Sample volume, liters	Total sample weight, µg	Concentration	
			Start	Stop			$\mu g/m^3$	Estimated TWA, $\mu g/m^3$
4/3/79	4	Operator; silver paste application	0938 1307	1225 1629	760	7.9	10.4	21.4
4/4/79	16	Operator; silver paste application	0846 1326	1158 1346	396	8.7	22.0	
4/4/79	25	Operator; silver paste application at larger machine	1347	1623	315	14.0	20.6	
4/4/79	24	Operator; silver paste	1350	1624	317	19.0	60.0	

TABLE E-3. SAMPLING SUMMARY FOR LEAD FROM CELL INTERCONNECTION SOLDERING AT PLANT E

Date in 1979, month/day	Sample No.	Sample description	Time		Sample volume, liters	Total sample weight, μg	Concentration	
			Start	Stop			$\mu g/m^3$	Estimated TWA, $\mu g/m^3$
4/3/79	5	Soldering operator; normal operation	1000 1305	1228 1629	738	<1	<1.3	
4/3/79	7	Area sample in interconnection central work area	1321	1631	401	4	10	
4/4/79	17	Soldering operator; normal operation	0850	1156	407	3	7.4	
4/4/79	18	Area sample in interconnection central work area	0850	1630	948	1	1.1	

TABLE E-4. SAMPLING SUMMARY FOR PARTICULATES FROM MODUAL LAMINATION AT PLANT E

Date in 1979, month/day	Sample No.	Sample description	Time		Sample volume, liters	Total sample weight, µg	Concentration	
			Start	Stop			Part, mg/m^3	Estimated TWA, mg/m^3
4/3/79	3	Model lamination operator; normal operation	0941 1259	1202 1630	698	0.06	0.09	
4/4/79	15	Model lamination operator; normal operation	0851 1420	1205 1623	647	0.12	0.19	

TABLE E-5. SAMPLING SUMMARY FOR TCF AND TCE FROM SOLVENT CLEANING AT PLANT E

Date in 1979, month/day	Sample No.	Sample description	Chemical measured	Time		Sample volume, liters	Total sample weight, μg	Concentration	
				Start	Stop			mg/m^3 (ppm)	Estimated TWA, mg/m^3 (ppm)
4/3/79	6	Module cleaning operator	TCF	0946	1257	37	554	15.0(2.4)	
			TCE	1336	1632		1229	33.2(6.1)	
4/3/79	12	Operator of washing crystal grower	TCF	1822	1906	8.8	77428	8800(1390)	
			TCE				1601	8.1(1.5)	
4/4/79	19	Module cleaning operator	TCF	0847	1340	29	789	27.2(4.3)	
			TCE				30497	1059(194)	
4/4/79	22	Same operator as at Sample 19	TCF	1343	1630	17	734	43.2(6.8)	33.1(5.2)
			TCE				6856	403(74)	812(149)
4/5/79	29	Area sample during washing of crystal grower	TCF	0048	0200	13	2731	210(33)	
			TCE				85	6.5(1.2)	

TABLE E-6. SAMPLING SUMMARY

Location or job title	Pollutant	No. of TWA determinations	Range	Mean	No. of short-term samples	Short-term peak
Ingot growing	Partic.	2	0.13-0.15 mg/m^3	0.14 mg/m^3	6	0.16 mg/m^3
Wafer slicing	Partic.	2	0.31-0.45 mg/m^3	0.38 mg/m^3	0	
Metallization operator	Silver	2	10.4-21.4 μg/m^3	15.9 μg/m^3	1	60 μg/m^3
Cell interconnection	Lead	2	<1.3 μg/m^3		2	10 μg/m^3
Module lamination	Partic.	2	0.09-0.19 mg/m^3	0.14 mg/m^3	0	
Module cleaning	TCE	2	6.1-149 ppm	77.5 ppm		
Ingot grower cleaning	TCF				2	1390 ppm

Wafer Etching and Cleaning

Wafers were cleaned in a laboratory-type hood. Face and control velocities were 53-61 m/min (175 to 200 ft/min) at the bottom of the hood opening and over the small cleaning tanks. Face velocities near the top of the opening were 23-30 m/min (75 to 100 ft/min). Tracer smoke indicated uniform air flow into the hood. The performance of this ventilation control was considered adequate.

Three relatively small dip tanks [0.6 m by 0.6 m (2 ft by 2 ft)] were provided with local exhaust ventilation by lateral slots integrally molded into the tank structure by the tank manufacturer. Slot inlet velocities averaged 305 to 366 m/min (1000 to 1200 ft/min) for each of the tanks. Tracer smoke indicated strong and uniform flow into the exhaust slots from several inches outside and around all tank edges and from about 30 cm (12 inches) above the tank. These controls were considered to be adequate.

A laboratory hood was also located at the end of the wet cleaning line for additional cleaning purposes. The average face velocity was measured to be 53-61 m/min (175 to 200 ft/min). This was also considered adequate.

The tanks and hood were vented by two separate systems, one for the two caustic tanks and one for the acid tank and hood. Plastic duct work was used for each system. Duct diameters were quite large, 2.5-m (8-ft) takeoffs, 30-cm (12-in.) branches, and 38-cm (15-in.) mains. Consequently, transport velocities were rather low. Condensation and drainage would seem likely. Appropriate facilities for draining the duct work should be provided. In future design of new systems, duct work should be sized to provide appropriate transfer velocity to minimize the potential hazard from liquids inside the duct work.

Diffusion Tubes

Equipment for diffusion-doping of silicon wafers was found to be state-of-the-art. The feed end of the tubes was located within a laminar flow hood which provided uniform downward draft of filtered room air. The hood operated with an excess of supply air to ensure that a slight outflow would be maintained. Air was exhausted from the bottom of this hood.

Local exhaust ventilation was provided at the "open" discharge end of each tube. Slight streams of "fume" emanating from the diffusion tubes were observed to flow directly into the local exhaust openings.

The controls and dopant inlet end of the diffusion system were totally enclosed and vented by exhaust.

Ventilation controls for the diffusion tubes were considered quite effective.

Metallization

Table E-2 presents the results of personal sampling for silver conducted by the operator of the metallization paste applicator. Two full-shift samples resulted in exposures of 10.4 and 20.6 $\mu g/m^3$ based upon a 2-1/2-hour sample. The current TLV and OSHA standard for silver exposure is 10 $\mu g/m^3$. Thus all samples exceeded this standard. It is recommended that local ventilation be installed on the paste applicator. The wafers pass through well enclosed firing ovens, which were vented by natural draft to the atmosphere for convection heat removal. Inflowing velocities at tunnel openings were generally less than 15 m (50 ft) per min. Terpineal, a mixture of isomers of $C_{10}H_{18}O$ used as a solvent in the silver paste, is driven off in the ovens. Although the odor of organic compounds was detected near the ovens, terpineal exposure of any operator appears unlikely to be significant.

Panel Assembly

Electrical connections were soldered onto each cell in the formation of a complete solar panel. Soldering tools were provided with small copper tubes mounted on the handle of the soldering iron, with the open end about 1.2 cm (1/2 in.) from the tip of the iron. The tubes were connected to a vacuum pump through a line running between the work tables. The vacuum pump discharged into the room.

This local exhaust system was not particularly effective for the capture of soldering/flux fumes. The level of control was significantly affected by the speed at which the soldering iron was moved from point to point. If done slowly, some visible "smoke" was removed; if done quickly, very little was removed. Control also appeared weaker at the farthest locations from the pump.

Table E-3 presents the results of personal and area sampling for lead from cell interconnection soldering. The personal samples showed exposures of less than 1.3 and 7.4 $\mu g/m^3$ and the corresponding area samples showed concentrations of 10 and 1.1 $\mu g/m^3$. The differences between personal and area sample concentrations are probably caused by different work patterns in the room. These concentrations are all well below the TLV for lead of 0.05 mg/m^3.

Solvent cleaning of finished modules resulted in full-shift exposures to TCE of 6.1 and 149 ppm. Corresponding TCF exposures were quite low. The TLV for TCE is 350 ppm. Although TCE levels were well below the standard, exposure could be reduced by improved operating practice.

General Ventilation

Three vertical ducts were dropped from evaporative coolers on the roof of the building to diffusers located about 3 m (10 feet) above the floor. These ducts were located in the central portion of the manufacturing plant.

The air supply/conditioning units were reportedly used only in warm weather to supply 100 percent outside air. No other air was forced into the plant, although the building was rather loosely constructed and outside doors were frequently left open. Air in the plant was found to be relatively still, with no dominant current.

The plant area was found to be at a static pressure, which was slightly negative with respect to the adjacent office areas. This was considered desirable, because it provided some clean makeup air to the plant and prevented contaminant flow into the offices from the plant.

CONCLUSIONS

No significant health hazards were found during this survey. The only elevated exposures were to silver during the metallization process and TCF during cleaning of the ingot grower. Exposures in both areas could apparently be readily reduced to acceptable levels.

No free crystalline silicon was found in the ingot growing or slicing areas.

Local and general ventilation at Plant E were considered to be generally adequate for health hazard control.

PLANT F: SILICON MODULE PRODUCER AND R&D FACILITY WALK-THROUGH SURVEY

SUMMARY OF SURVEY FINDINGS

Plant F is conducting research on a wide range of photovoltaic process technologies, as well as producing finished modules. Polycrystalline and single-crystal silicon production, as well as wafer production, are considered to be a part of the far larger semiconductor area.

Industrial hygiene controls appeared uniformly excellent. Chemical handling and accident prevention systems appear to present an industry model.

PLANT DESCRIPTION

This facility is primarily devoted to semiconductor manufacturing. Research and development work in photovoltaics began in early 1974; production began in the spring of 1977. The photovoltaic area, defined as starting with silicon wafer material, is located in one building.

DESCRIPTION OF WORK FORCE

Roughly two-thirds of photovoltaic operators are male. Approximately 84 percent work on the day shift; the remainder are on the afternoon shift. An employment record on each operator is maintained by the Personnel Department. Medical and accident records are kept by the nurse at each work location.

MEDICAL, HEALTH, AND SAFETY PROGRAM

The Safety Manager and Safety Engineer serve as plant industrial hygienists. They check all new equipment before installation or operation to evaluate industrial hygiene controls. Also, extensive sampling and ventilation measurements are made.

The Staff Medical Clinic provides medical care, and full-time nurses are located throughout the plant.

New employees are given physical examinations as required, and examinations are repeated on an annual basis.

PROCESS DESCRIPTION

The current emphasis of Plant F in the solar photovoltaic industry is largely at the R&D level. This description will consider both production processes and developmental processes. The silicon is produced by the Semiconductor Group, whereas the scope of photovoltaic production is from wafer to finished module.

Polycrystalline Silicon Production

Polycrystalline silicon is produced from trichlorosilane ($HSiCl_3$) in a separate building and is used primarily in the semiconductor area. The $HSiCl_3$ is stored in nitrogen-covered tanks outside the process building. Polycrystalline silicon is formed in chambers by the decomposition of $HSiCl_3$ saturated in an H_2 stream. The bell jar chambers are operated at 1100°C and 7 in. H_2O pressure for about 230 hours per batch cycle. This process is totally closed and highly automated; the gas from the chambers which contains contaminants, (notably HCl and chlorosilanes), is filtered, compressed to 4.4 atm, and purified before recycling. Purification involves charcoal adsorption to remove HCl and cooling and condensation to condense heavy ends. Parallel charcoal chambers are used, because the charcoal is regenerated every 6 hours.

The ventilation rate of the chamber room was generally very great. The flow pattern was from floor grating up out through ceiling louvres.

Four shutdown systems were reportedly installed for emergencies. If the chamber glass breaks and fire results, the feed gas and exhaust lines are closed.

Few operators were observed in this area.

Crystal Pulling and Wafer Cutting

Crystal pulling and wafer cutting were considered to be part of the semiconductor area and were not surveyed in depth. Standard Czochralski single-crystal pullers and single-blade wafer cutters were used.

Alternative technology being developed by Plant F consists of a ribbon growth technique with laser remelt of polycrystalline silicon from silicon vapor deposition. The process sequence consists of preheat of the silicon ribbon, exposure to two CO_2 laser beams, and postheat. The heating stages remove stress from the ribbon, and the lasers melt the ribbon at the exposed area to form larger crystal grains. The laser rating was 1.2 kW. The growth rate was 10 cm (4 in.) per hour.

This process was totally enclosed and shielded.

Wafer Cleaning and Etching

Wafer cleaning and etching operations are primarily for use in the semiconductor area. Similar treatment sequences, however, are followed for photovoltaics.

After sawing, wafers are wet-etched in NaOH and rinsed to remove saw damage. Wafers in plastic cassettes are immersed in an acidic solution containing acetic acid, HF, and HNO_3. Cleaning may be performed in a mixture of H_2O_2 and H_2SO_4. All cleaning and etching operations are located in laminar flow hoods. Hoods use two filter grades for particulate removal and are equipped with hood failure alarms, which turn off the laminar flow blower and activate both sound and light alarms to warn personnel that the exhaust has failed. Standard procedure is to evacuate the entire area until the exhaust is restored. After etching or cleaning, wafers are rinsed and dried by centrifuge.

Texture Etching

Plant F is developing photoresist techniques to mask the wafer during texture etching, when only one side is to be etched. The photoresist process involves putting a photoresist material in a xylene-based solvent into an exhausted chamber, while the wafer is spinning to remove excess liquid. Exposure of the wafer to an ultraviolet lamp develops the photoresist chemicals on one side and allows dissolution of undeveloped photoresist chemicals from the other side. This process occurs in a laminar flow down-draft hood with fail-safe exhaust. The wafer is then given a wet etch consisting of a heated KOH-based bath for texturing. A UV light is used in this work area.

Junction Formation

The open-tube diffusion process is used for junction formation in current production. Work on ion implantation is at a near-term developmental level.

Seven diffusion furnaces were operated primarily for semiconductor production. After inspection for defects, wafers in cassettes are loaded manually into tube furnaces. The diffusion process requires about 90 minutes per cycle, in which the furnace temperature is increased from about 480° to 540°C (900° to 1000°F) in various atmospheres. For example, pure H_2 and O_2 are metered in to form a steam and to form an oxide layer 10,000 to 14,000 A thick on the wafers. Dopants used include BCl_3 and PH_3. The operating cycle is automatically controlled. The silicon nitride surface coating is formed by thermal decomposition of ammonia and dichlorosilane in the enclosed furnace. The operating cycle is automatically controlled. All cycles are purged with either N_2 or argon.

Pressure cylinders of O_2, H_2, N_2, BCl_3, and PH_3 are stored at the back of the furnace assemblies with ventilation hoods and equipped with low-ventilation-flow alarms. The inlets of the tube furnaces are equipped with side-draw ventilation.

Ion implantation also operates on a fully automated cycle, requiring only the operator to load and unload cassettes. This is a much faster cycle, requiring only a few minutes. Implantation occurs in a vacuum chamber with gas (PH_3, BF_3, or AsH_3) or vaporized solids (Al) as dopant sources. The wafers are then subjected to a high-temperature annealing step involving a pulsing source or a furnace at 900°C (1650°F) maximum. Some metal oxide formation occurs during implantation and is removed with wet chemistry.

Concentrations of all dopant exposures measured have been less than 1 ppm.

Metallization

The metallization pattern is formed by silk screen or photoresist. Silk screening consists of forming silk screen patterns on both sides with a petroleum wax in an isopropyl alcohol solvent, baking the wax dry in a vented low-temperature oven, and etching the exposed silicon nitride surfaces with a mixture of HF and ammonium fluoride. This process is conducted in a laminar flow exhaust hood. This process is reportedly expensive because it is labor intensive and required high chemical usage.

Plasma ionization was reportedly a more promising etching approach. In this process, a mechanical mask is applied to the wafers, and they are exposed to CF_4 plasma ionized in an RF field. This process is closed and vented. This process may be extended to texture etching.

After pattern definition, palladium is plated from two different baths to form a 0.05-micrometer barrier layer, and wafers are placed into a "sintering tube furnace," in which palladium and silicon are "alloyed" onto the surface of the wafer. Each tube has an exhaust hood at the inlet opening and is vented. Cells are then dipped in an electrolytic bath of nickel, palladium, and copper salts. These operations are conducted in laboratory hoods, and each operator wears an impervious frock and gloves during all plating operations. Cells are then dried and dipped in a flux and a nickel-selective solder (Pb/Sn).

Module Assembly

Two parallel and identical process lines are used for panel assembly and testing. Wafers are placed by hand on copper-plated panels and then on a hotplate. The hotplate is exhaust-ventilated by a slotted backdraft hood. Final alignment, inspection, and testing are conducted in front of similar hoods. Hand soldering may occasionally be done during inspection and testing.

Panels are then placed in a degreaser containing isopropanol and methylene chloride. The degreaser is equipped with a vapor trap and with a local exhaust ventilation system consisting of three backdraft slots. Solvent vapor levels in the degreaser area are continuously monitored, reportedly with a combustible gas detector, which signals audibly when explosive mixtures are approached.

The panels are placed in trays, and a glass cover is placed over them. Silicon "gel" is injected between the glass cover and the panel, and the tray is placed in a vented oven to cure the silicon.

The trays are dismantled, and the finished panels are removed and placed in final mounting frames. The trays are wiped clean with 1,1,1 trichloroethane. These steps are carried out on a ventilated table, with exhaust slots around the full perimeter.

SURVEY OBSERVATIONS

Polycrystalline Silicon Production

The process of producing polycrystalline silicon appeared highly automated. The major potential for worker exposure appears to be from HCl in the event of bell jar breakage or maintenance operations if residual chlorosilane remains in opened equipment. This area, however, was not inspected in sufficient detail for adequate evaluation.

Wafer Cleaning and Etching

Wet chemical cleaning and etching processes are conducted in laminar flow exhaust hoods. Room air is drawn into a plenum at the top of the hood and supplied to the hood interior by a laminar downdraft. Air is exhausted through a plenum in the bottom of the hood, with sufficient flowrates to ensure a uniform indraft through the front opening of the hood. Each hood is also fitted with a static pressure alarm that signals audibly in the event of fan failure.

All laboratory hoods have been checked for proper control velocities and airflow patterns by Plant F safety engineers and carry a dated approval sticker.

No chemicals are poured directly into the sink drain. All acids and other waste chemicals are aspirated and diluted with water before entering the drain.

All exhaust is passed through scrubbers before venting to the atmosphere.

Both photoresist and plasma etching operations located in laboratory hoods appeared well ventilated.

Ribbon Technology

Lasers, located in a separate room, are used in a process for growing crystalline silicon ribbons. All chambers have windows designed to adsorb all laser light that might be reflected toward them. Additionally, goggles are worn by all personnel when a laser is operating. Warning lights and an automatic lock prevent anyone from entering the process room when a laser is operating, unless specifically admitted by a technician. This operation appeared well controlled.

Junction Formation

The diffusion furnaces appeared well controlled. Both front wafer access areas and back chemical injection areas appeared well vented. Cylinders for the doping gases (phosphine, arsine, boron trichloride, and others) are stored inside a ventilated enclosure equipped with a static pressure alarm that shuts off all gas cylinders in the event of an exhaust fan failure.

Ion implantation appeared very well controlled. One operator feeds in the silicon wafers and interacts with the machine only through the control panel. The entire machine is enclosed and vented to the atmosphere. Cylinders of doping gases are stored in a manner similar to that described for diffusion.

After ion implantation, wafers are placed in high-temperature furnace tubes and are exposed to various toxic gases, such as ammonia, phosphine, and chlorosilanes. The furnace is vented to the atmosphere, and the toxic gases are stored in an exhaust-vented hood equipped with a static pressure alarm and automatic cylinder shut-off devices.

Chemicals Handling

All chemicals are supplied to the R&D laboratory through the corridor adjacent to one of the inner walls. Chemicals are placed in ventilated lockers that open to the hallway and are labeled for each type of material to be stored inside. These lockers also open to the laboratory, so that the number of people entering the laboratory is kept to a minimum. Cabinets are 2-hour fire-rated and designed specifically for chemical storage safety.

Metallization

Metallization processes are conducted inside laboratory hoods, which were tested and approved by the plant Safety Department. No further control would be anticipated.

Module Assembly

All of the local exhaust ventilation controls seemed to be well designed. They have been tested and approved by the Safety Department.

DISCUSSION

The facilities and processes at Plant F involve the production of solar panels beginning with silicon wafers and were found to be controlled very well for industrial hygiene. Ventilation controls were well designed and were tested by competent and concerned safety engineers. Polycrystalline and single-crystalline silicon production areas were not inspected in sufficient detail for comment.

The approach to ventilation control and chemical handling evident throughout the survey and stated by the plant Safety Manager was to provide complete control for every operation and every possible air contaminant. This approach is effective and the survey indicates that by most standards Plant F would be considered a model to which other facilities might aspire.

Alternative technology being developed by Plant F consists of a ribbon growth technique with laser remelt of polycrystalline silicon from silicon vapor deposition. The process sequence consists of preheat of the silicon ribbon, exposure to two CO_2 laser beams, and postheat. The heating stages remove stress from the ribbon, and the lasers melt the ribbon at the exposed area to form larger crystal grains. The laser rating was 1.2 kW. The growth rate was 10 cm (4 in.) per hour.

This process was totally enclosed and shielded.

Wafer Cleaning and Etching

Wafer cleaning and etching operations are primarily for use in the semiconductor area. Similar treatment sequences, however, are followed for photovoltaics.

After sawing, wafers are wet-etched in NaOH and rinsed to remove saw damage. Wafers in plastic cassettes are immersed in an acidic solution containing acetic acid, HF, and HNO_3. Cleaning may be performed in a mixture of H_2O_2 and H_2SO_4. All cleaning and etching operations are located in laminar flow hoods. Hoods use two filter grades for particulate removal and are equipped with hood failure alarms, which turn off the laminar flow blower and activate both sound and light alarms to warn personnel that the exhaust has failed. Standard procedure is to evacuate the entire area until the exhaust is restored. After etching or cleaning, wafers are rinsed and dried by centrifuge.

Texture Etching

Plant F is developing photoresist techniques to mask the wafer during texture etching, when only one side is to be etched. The photoresist process involves putting a photoresist material in a xylene-based solvent into an exhausted chamber, while the wafer is spinning to remove excess liquid. Exposure of the wafer to an ultraviolet lamp develops the photoresist chemicals on one side and allows dissolution of undeveloped photoresist chemicals from the other side. This process occurs in a laminar flow down-draft hood with fail-safe exhaust. The wafer is then given a wet etch consisting of a heated KOH-based bath for texturing. A UV light is used in this work area.

Junction Formation

The open-tube diffusion process is used for junction formation in current production. Work on ion implantation is at a near-term developmental level.

PLANT G: SILICON MODULE PRODUCER--WALK-THROUGH SURVEY

SUMMARY OF SURVEY FINDINGS

Plant G produces finished solar modules and arrays using silicon wafers purchased from other companies. Battery voltage regulators, which are assembled at the plant, are included in the module. Equipment and processes requiring local ventilation include the diffusion furnaces, acid etching, electroless plating, acid wash, solder dip, acid-etch of wafer edges, solvent mask removal, cell tabbing, and finish coating. Although this is a small operation, there are many wet chemical operations requiring controls, principally acid or solvent process. Because of the diversity of materials handled and the labor-intensive nature of most of the operations, it is recommended that routine industrial hygiene surveys be conducted and that all process changes be reviewed from the standpoint of industrial hygiene.

PLANT DESCRIPTION

Although all finished cells are produced by a similar process sequence, two main module designs are used: a glass and aluminum frame design and a molded fiberglass and silicon-resin design. Production at this facility started in 1977.

DESCRIPTION OF WORK FORCE

The plant operates 5 days a week on day shift only. There are a total of 20 operating personnel, half of whom are women. The operating personnel come from a range of age groups and work backgrounds. New employees complete a job application including work history and are given a physical examination.

MEDICAL, HEALTH, AND SAFETY PROGRAM

Plant G does not employ an industrial hygienist but has access to one as needed. A comprehensive industrial hygiene survey was conducted in October 1978. This included personal sampling for metals and solvents as well as measurements of airflow in all local ventilation systems.

A private physican is retained part-time to provide physical examinations and routine and emergency medical care.

PRODUCTION PROCESSES

Plant G produces finished modules and array assemblies starting from silicon wafers. Finished modules are encased either in silicone resin with fiberglass molding or in a glass front and mylar backing with an aluminum frame. Assemblies include battery voltage regulators. The sequence of wafer processing is presented below:

1. Junction formation by diffusion furnace
2. Acid etching and water rinsing
3. Cleaning with alcohol and ovendrying
4. Metallization pattern
5. Acid washing and water rinsing
6. Metallization
7. Water rinsing, alcohol cleanup, ovendrying
8. Dipping wafer in solder baths
9. Masking front and back of wafer
10. Acid etching wafer edges
11. Removal of mask
12. Electrical testing
13. Tabbing cells
14. Stringing cell interconnections
15. Module encapsulation
16. Assembly of battery voltage regulator
17. Array assembly

Wafer Diffusion

The silicon wafers are first doped with boron in diffusion furnaces to form a pn junction. Four tube furnaces, operated on an automatic time-temperature sequence are used for this purpose. Wafers are placed back to back on metal trays and loaded into a furnace. The boron gas is supplied to each diffusion furnace by a separate boron gas cylinder located nearby. A gas cylinder typically lasts about 4 weeks.

Side-draw local ventilation is provided near the inlet of each tube together with a downdraft airflow at the front assembly. Exhaust air is water scrubbed prior to discharge.

Chemical Etching

Wafers are placed in cassettes and dipped sequentially in an acid etch bath, two water rinse baths, and an isopropyl alcohol cleaning solution. These operations are performed under laboratory hoods, and the acid etch bath is equipped with a full-front plexiglass shield. Cassettes are then loaded into a low-temperature, vented drying oven.

Metallization

Patterning of a conducting grid prior to metallization is physically applied using a chemical resist. The chemical resist contains a C_8-C_{12} hydrocarbon solvent vehicle.

The wafers in cassettes pass through a series of baths to form a metallization layer by electroless plating. The baths, in sequence, are a dilute acid wash, a water rinse, plating baths, and an isopropyl alcohol bath for cleaning and drying. The baths are all located in a laboratory hood except for the alcohol bath, which is located in the open room without local ventilation.

Wafers are then dipped in Pb/Sn solder baths. These baths are equipped with backdraft slots.

Etching of Wafer Edges

The metallized wafers are masked, both in front and back except for the wafer periphery.

Next, wafers in cassettes are given an acid etch and two water rinses. This is done in a laboratory hood.

The wafers are dipped sequentially in solvent baths to remove mask. The baths are (equipped with backdraft slots) to remove the wax. The solvent is emptied each day into waste drums.

Individual cells are tested using a standard light source in an enclosed test chamber.

Module Assembly

Assembly consists of tabbing cells, stringing them in the desired module electrical circuit, encapsulating in the glass or resin line, and connecting battery voltage regulators.

Individual cells are placed in a template and pretinned, and electrical interconnection tabs are soldered onto the back surface with a 60/40 lead/tin solder. Slot ventilation is provided behind the work stations. Next, tabbed cells are strung together in the module pattern. In this operation, the tabs of each cell are soldered to the front edge of the adjacent cells. The completed string of cells is then dipped in a water wash tank to remove any loose dirt on its surface.

For glass-front module production, a string of cells on a mylar sheet is encapsulated by spraying the front of the cells with a GE primer, applying the front glass, and adding a silicone resin layer for adherence. A silicone-rubber gasket is placed around the unit, and it is inserted in an aluminum frame. Up to six modules are connected in an array, which includes structural members, legs, and foot pads.

For the silicone-resin product line, a molded fiberglass base with structural member design is used. The base has indentations in the front to accommodate the individual cells. Silicone resin is poured over the front surface, and the module is cured overnight on a level rack. The rack is located in a central work area.

Plant G also assembles and installs battery voltage regulators on modules. The voltage regulator assembly includes component soldering with a standard lead solder. A cable diode is installed on the glass units and sealed with a two-component epoxy resin. On the resin line, the junction box is sealed in the same two-component epoxy resin.

The resin line is then given a finish coating of DOW R-4-7117 sealer to give a smoother resin surface. The coating, which contains xylene solvent, is applied in a paint spray booth with a standard pneumatic paint spray gun. A separate room is provided for this operation.

Waste Treatment and Handling

Emissions from acid hoods are all vented to a water scrubber in an adjoining room. (At the time of the survey, a separate alkaline prescrubber was being tested on the gas vented from the diffusion furnace.) Liquid wastes are stored in tanks outside the building and are hauled away to a private contractor.

SURVEY OBSERVATIONS AND RECOMMENDATIONS

Slice Diffusion

Cylinders of dopant gas kept near the furnace should be hooded and vented to prevent the release of emissions from an accidental rapture.

A buildup of white solid material at the inlet of each furnace tube indicates that the ventilation system should be checked regularly for the possibility of increased line resistance.

Tests using bubbler solution to measure HCl at the furnace entrance reportedly showed low levels. The side-vent airflow rate was also tested.

Chemical Etching

No problems were observed. Acids such as nitric, hydrofluoric, acetic, or their mixtures, were used.

Metallization

The screen-printing devices are manually operated and lack ventilation. A back-draw local ventilation should be installed. Tests for solvents using charcoal tubes reportedly showed low exposure levels. Also, the plated cells are dipped in an isopropyl alcohol bath without ventilation. This operation should be located in a hood or have side-draw ventilation.

Etching of the Wafer Edges

Removal of the mask in 1,1,1-trichloroethane baths appeared to be a messy operation. It was reported that the back-draw slots had been tested and found to be adequate.

Because of the number of different solvents used in this small work area, a hood might ensure more complete solvent containment.

Module Assembly

Curing of silicone and epoxy resin was done in the general work area. Standards of good practice dictate that these operations be done in a separate room vented directly to the outdoors.

The paint spray booth appeared well designed.

Operating Procedures

Few processes were observed in operation; as a result, comments on operating procedure and work practice cannot be made.

PLANT H: SILICON MODULE PRODUCER
WALK-THROUGH SURVEY

SUMMARY

A walk-through industrial hygiene survey of Plant H was performed. A process description along with observations of engineering controls, work practices or other precautions taken, are presented for each operation in the plant. This facility primarily was found to lack a well organized environmental engineering control program. Example and suggestions to that effect are offered.

PLANT DESCRIPTION

Plant H is located in a light industrial complex single story building. Plant H is an original tenant in this 40,000 ft^2 facility which opened in August, 1973. Recently, the company became the sole occupant.

The facility is centrally heated and cooled through a common recirculating system. Locally exhausted ventilation is provided at certain locations. The process has been partitioned into three major areas; shipping and receiving, primary cell production, and array assembly.

DESCRIPTION OF WORKFORCE

Plant H employs approximately 75-80 operating personnel, about half of whom are women. More than twice that number are employed in auxiliary capacities. The production line operates on a 15-hour staggered work shift. The majority of the operating personnel are under 30 years of age and have no predominant work experience.

MEDICAL, HEALTH, AND SAFETY PROGRAM

The Manager and Chief Scientist, heads the safety program at Plant H. Production supervisors are also responsible for encouraging safety measures. No one is known to currently have received formal instruction in safety or first aid.

The company's insurance carrier provides periodic inspections by a safety/industrial hygiene professional. However, no measurements, other than those taken by the Maryland Occupational Safety and Health Program, have been taken.

Plant H requires no pre-employment or other periodic medical examinations. The company retains no nurse or medical doctor. The facility is, however, located within ten miles of two hospitals and both can be used for emergency treatment.

PRODUCTION PROCESSES

Plant H produces finished modules and array assemblies for a variety of customer needs. Basically, the process calls for the following steps to be taken:

- Diffusion furnace junction formation
- Application of photochemical resist pattern for grid placement
- Evaporative metallization
- Remove resist
- Electroplate conducting grid
- Apply antireflection coating
- Solder tabs and interconnect cells in module
- Encapsulate cells in module
- Module assembly

SLICE PREPARATION

The company buys most of its p-doped silicon as sliced wafers but has some capability to slice their own. Incoming wafers are cleaned with a 20 percent sodium hydroxide solution and may be etched with a mixed acid if they show work damage. Caustic and acid baths are located under hooded exhaust. The wafers are transported from each bath in wafer carrying baskets. Operators wear natural latex gloves when handling the baskets.

SLICE DIFFUSION

The cleaned wafers are next manually transferred to a small room housing tube furnaces used for phosphorus diffusion. Phosphine is used for formation of the n-type layer in addition to use of an inert carrier gas and oxygen. Gas cylinders were retained on an adjacent side wall. Phosphine cylinders are changed infrequently. This room is under general building ventilation and the air recirculated. The diffusion furnace parts, however, are locally exhausted to the outside. This is not a labor intensive operation.

GRID PLACEMENT

The wafers, now with a p-n function, are ready for electrical conduction grid placement. This process utilizes a proprietary photo chemical resist where the solvent based resist is spun on, belt-oven dried, and exposure under violet light alters the resist in the grid pattern. The spin-on table as well as the ultraviolet lamp apparatus are both exhaust ventilated to control solvent vapors and ozone/nitrogen oxide formations, respectively. Protective lenses which absorb ultraviolet light are worn by the ultraviolet lamp operator and natural latex gloves by the spin-on resist operator. The unpolymerized polymer is then rinsed away with potassium hydroxide and water.

METALLIZATION

Metallization of the surface conductive grid and back surface electrode is performed through sequential evaporation of titanium, palladium, and silver. The back surface is coated with aluminum. The bell casing is lined with foil, thus greatly reducing deposition on the casing wall as well as maintenance problems. This operation was not observed between cycles but would support good practice in reducing metal dust exposure to the maintenance operator.

After metal evaporation, the remaining chemical resist is removed in an acetone bath. This operation was also not observed but appeared well engineered to minimize operator exposure.

Next the evaporated grid is thickened by submerging the wafer in a cyanide electroplating bath. The baths are covered while plating occurs and exhaust ventilated to the outside. This is a full time, one operator job. The operator must wear protective gloves, apron, and safety glasses. This operation has reportedly caused one dermatitis case which resulted in the operators' transferal. Emissions consist primarily of potassium cyanide and carbon dioxide. Waste solution is disposed by contract pickup.

ANTIREFLECTION COATING

Finally, a tantalum oxide antireflection coating is deposited by electron beam gun. This is also lined with foil to reduce wall deposition. The cells then pass through a belt conveyor oven to sinter the grid contacts.

Periodically, a cell is performance tested under a tungsten filament lamp.

TABBING AND STRINGING

Before encapsulation in the cell array, electrical tabs are soldered onto each cell with a common 60/40 lead-tin solder containing a rosin core flux. Stringing, or cell interconnection, is also performed by the same operator. The soldered cells are cleaned in a proprietary flux remover solution and isopropyl alcohol. The solvent baths are located under an enclosed ventilated hood. Recent spot sampling indicated excellent containment of solvent emissions.

MODULE ASSEMBLY

Prior to encapsulation in clear polysilicon rubber, a proprietary primer is applied to the polyester back surface sheeting. Application of the primer is performed under a hood to reduce operator exposure to irritating acid fumes. The primer is further dried in an oven vented to the outside.

The primed polyester sheet and wafers are placed in an aluminum frame on a conveyor. Polysilicon rubber resin is applied to the module and cured in a belt oven. The oven is not vented since no toxic vapors are known to be given off. The module is removed from the conveyor and a glass plate is finally installed and sealed in with polysilicon rubber. The module is now finished.

SURVEY OBSERVATIONS AND RECOMMENDATIONS

Diffusion Junction Formation

The diffusion furnace room should be segregated on its own ventilation system. Gas cylinders would be better located in a separate room outside the operating area or be located in their present location but equipped with an alarm/fail safe system and under hooded exhaust.

Resist Patterning

While this operation was somewhat isolated within the building, it appeared inadequately ventilated. The unventilated drying oven is probably a primary source of solvent based resin volatilization. This operation should also be on a separate room ventilation system with adequate makeup air supplied. Personal monitoring of organic solvent, ozone and nitric oxides is recommended.

Evaporative Metallization

This appeared to be a well controlled operation. However, maintenance functions were not observed and this is likely to present the greatest potential exposure to airborne metal dusts.

Resist Removal

The ultrasonic acetone bath appears to require little operator attention and appeared well controlled.

Electroplating

This operation was located in the general primary cell production area. Each bath was covered by a lid with a flexible tube exhaust hose to the roof. A better practice would be to also isolate this potentially hazardous operation and locate the electroplating baths under laboratory type hoods or draw slot exhaust.

Applying Antireflection Coating

No apparent problems were observed. Again, the greatest likelihood of concern from an industrial hygiene viewpoint would be during maintenance operations. Such operations were not observed.

Soldering

The cell tabbing and stringing operation was performed without benefit of local ventilation. This operation should be monitored. Good practice would warrant local ventilation to minimize metal and flux fume exposure.

The solder flux dip tank appeared well designed and should present no problem.

Encapsulation

No apparently toxic agents were used other than a commercially available priming agent. This agent is usually applied under a hooded exhaust which appeared adequately designed.

General

General housekeeping appeared marginal in some areas. An overcrowding condition existing in this plant would contribute to this situation.

Recirculation of plant contaminants should be prevented where possible. Potentially toxic areas should be segregated. Fail safe/alarm indicators should be installed on ventilation systems controlling hazardous operations in enclosing areas.

A number of eye injuries were noted in the accident records and reported as a problem by management. Ways to increase employee compliance with good work practices include: (1) publicizing injuries so all will know, (2) take a hard line and publicize the company's policy, and (3) post hazardous warning signs and labels in conspicuous places. At least one employee, preferably a supervisor, should be present at all times, who has had formal first aid training. That person should be knowledgeable particularly with first aid procedures associated with the company's common working hazards.

Preserving employee health helps to improve morale, prevent lost time from work, maintain production, and reduce the cost of compensation benefits.

PLANT I: SILICON MODULE PROCEDURE
WALK-THROUGH SURVEY

SUMMARY OF SURVEY FINDINGS

Plant I produces finished silicon solar panels starting with ingot growing. Most operations are well controlled with few routine health hazards observed.

PLANT DESCRIPTION

Plant I occupies 47,000 ft^2 of space in one building. Operations began at the present location in the spring of 1975. The emphasis has been in the space solar photovoltaic area. Currently, Plant I produces silicon cells and modules and photosensors.

DESCRIPTION OF THE WORK FORCE

Plant I employs approximately 100 production workers. All are women over 30 years of age, mainly with long seniority. Most production occurs on the day shift.

A safety officer from the head office is responsible for industrial hygiene at this facility, although no measurements are routinely taken.

All new employees are given a physical examination, and subsequent examinations are provided on a voluntary basis. No severe lost-time accidents or trends in accidents were reported.

PRODUCTION PROCESSES

Ingot Growing

Two Czochralski units for growing silicon crystals operate in a separate room. Each unit produces a rod 7.6 cm (3 in.) in diameter in about 10 hours. A total of four rods are produced every day. Each batch includes a boron dopant. Crucibles are disposed of after each cycle. The vapor space around the crucibles is blanketed with argon under a slight positive pressure during operation. This results in the deposition of a fine silicon oxide layer on the inner wall of the chamber. This layer is removed with a dry towel and carefully wiped clean before the next cycle. Only two or three workers are located in this area.

Ingot Slicing

Some ingots are mechanically ground to yield a smooth cylinder surface of uniform diameter. Two Siltec single-blade diamond cutters are used. This is a 24-hour-a-day operation. The cutter is lubricated with water, and the lubrications and kerf loss flow to an underflow drum with a large buildup of solids. The saw waste or kerf loss is disposed of periodically. The operation is highly automated and requires only one or two workers. Wafers are then cleaned with detergent.

Diffusion Junction Formation

Four tube furnaces are operated to apply a layer of N-doped material on the wafers. The chemical vapor deposition of phosphorus in an open-tube furnace constitutes the main production process for diffusion junction formation. Each furnace contains eight tubes in which a tray of wafers is placed. The furnaces operate on 25-minute cycles at about 165°C (900°F) in an argon atmosphere. For a short period during the cycle, oxygen is bubbled through a closed container of phosphorus oxychloride ($POCl_3$) and introduced into the tubes.

Wafer Etching and Cleaning Operations

Wafers are cleaned in sequential hooded baths of sulfuric acid and nitric acid solutions followed by water rinse. These operations are followed by centrifugal rinsing and drying. Wafers in trays were transferred manually between operations.

Etching is done after the photoresist is applied. Wafers are placed in a hooded bath containing sulfuric acid and hydrogen peroxide solutions and then rinsed.

Solvents, including acetone and isopropylalcohol, are used in the etching and tube furnace areas.

Wafer Contact Application

Contacts are applied to wafers by three different techniques. A separate room is used for these operations.

An electron beam gun applies layers of titanium, pallatium, and silver in sequential operations. The apparatus is a 60-cm (24-in.) dome, and the beam gun moves in planetary rotation to contact the wafers, which are fastened in stationary positions. A mask support is positioned on the wafers to give the photoresist pattern.

The second technique is a similar electron beam gun operation. Coatings of titanium dioxide and aluminium oxide are applied to concentrator cells and space cells.

The third technique involves evaporating silicon oxide in evacuated bell jars. A thin layer of SiO is deposited on the cell upper surface at 315°C (600°F), and a nitrogen atmosphere is maintained in the bell jars. The bell jars are periodically cleaned with a nitric acid solution to remove oxide buildup.

After contact application, the wafers are passed through an oven to sinter the contacts. The oven was operated at 600°C (1110°F) and was maintained in a hydrogen atmosphere internally. A nitrogen curtain was at each end of the oven.

Solder Applications and Panel Assembly

Solder baths coat cells only on silver contacts. The solder (a mixture of silver, tin, and lead) is in small rectangular baths with slot ventilation at the back surface.

Although Plant I makes designs for several types of solar photovoltaic panels, the standard one consists of 36 cells and is rated at 24 watts. Cells are mounted on a Mylar sheet with a white backing. A front glass plate is used in the frame, and a polyvinyl butyrate sheet is molded onto the back. This latter operation is performed at another company location.

Modules are made with three main modifications. Cells may be coated with a mixture of aluminum and titanium, with silicon oxide, or with a white surface of aluminum-titanium and silver. Overall, this operation is very labor intensive.

SURVEY OBSERVATIONS

Crystal Growing

The environment for crystal growing is very clean. Only during cleaning of the units to remove silicon oxide is potential work exposure significant. Only area ventilation is used.

Ingot Slicing

Ingot slicing did not appear to generate a significant quantity of entrained particulate, and the noise level was quite low. Wafer detergent cleaning, however, was poorly hooded.

Diffusion Junction Formation

Workers are involved with diffusion junction formation only during loading and unloading of wafers. Side-draw ventilation at the front end of the tubes exhausts vapor, notably $POCl_3$. The $POCl_3$ is contained in a scaled quartz bubbler. The threaded couplings are punctured only when the connecting tubing is assembled. The $POCl_3$ bubbler is housed at the back of the furnace, and the chamber is vented.

Diffusion junction formation appeared to be a well controlled operation.

Wafer Etching and Cleaning Operations

All etching operations were loaded in laboratory-type hoods. Air flowed in and down around the baths. Workers wore protective clothing and gloves.

Solvents in cans were sitting out; some with spouts open. A strong acetone odor was in this area.

A separate acid mix room was used to make up acid solutions and transfer acid solutions from large drums to 19-liter (5-gallon) cans. Although three hoods were in place, this room appeared inadequately ventilated.

Wafer Contact Application

The environment for wafer contact application was very clean, with few or no emissions during operation of the units. Workers manually applied mask supports, making operation rather labor intensive. Cleaning bell jars and surfaces of other vessels may be the major operation that could expose workers to toxic materials.

Solder Application and Panel Assembly

Most operations connected with solder application and panel assembly are labor intensive. Such operations, however, were not performed at the time of visit. Most of the workers in this area were finishing or assembling semiconductor or space solar cell units.

COMMENTS

Generally the work environments were very clean. Only in the wafer etching and cleaning area, where solvent vapor was detected, were potential health hazards observed. This area also appeared to present the greatest potential for accidental acid or caustic splashes or vapor exposure resulting from ventilation failure.

If additional industrial hygiene work is undertaken, the following should be considered: measuring air flow through all hoods; sampling for particulates in all major work areas; spot sampling for solvent vapor concentrations in the wafer cleaning area; and reviewing fail-safe procedures for ventilation systems, etching and cleaning baths, and vacuum systems.

PLANT J: AMORPHOUS SILICON R&D FACILITY
WALK-THROUGH SURVEY

SUMMARY OF SURVEY FINDINGS

Plant J is presently involved in the research and development of thin-film amorphous silicon (a-Si) solar cells, in addition to various other photovoltaic devices. The goal of Plant J is to reduce the costs of manufacturing a-Si solar cells to about $0.30 to $0.40 per peak watt and to maintain a cell efficiency of at least 5 percent. Although all apparatuses and processes observed on this survey were strictly on a batch-type, laboratory scale, a system allowing more continuous production of a-Si photovoltaic cells is being constructed for use in various areas of research. The main processes observed on this survey were RF-induced glow discharge and sputter deposition. Although a variety of materials were used, most were used in extremely small quantities and are controlled very closely to minimize waste. Local ventilation was provided for the vacuum deposition chambers and for all containers of toxic gases. For the operations observed, safety precautions appeared adequate.

PLANT DESCRIPTION

Plant J first developed the a-Si solar cell in 1974. To reduce the cost of solar energy research, Plant J switched emphasis from single-crystal silicon cells to amorphous cells. At present, the plant has one contract with DOE for a-Si research.

DESCRIPTION OF WORK FORCE

Personnel involved in developing a-Si solar cells all have technical backgrounds and have done research for several years.

MEDICAL, HEALTH, AND SAFETY PROGRAMS

Plant J employs a Safety and Industrial Hygiene Officer on a permanent basis.

Industrial hygiene work is conducted at the divisional level not the corporate level. It was indicated that if industrial hygiene concerns fell outside the qualifications of the Safety Officer, then assistance would be obtained from outside Plant J.

The Safety Officer takes responsibility to see that ventilation systems are checked annually; checks include air sampling and noise and ventilation measuring. Shipping, storing, and handling of all chemicals and gases are also supervised by the Safety Officer.

EXISTING PRODUCTION PROCESS

The following description of processes involved in fabrication of a-Si cells is based on a walk-through survey of the facilities and on articles received from Plant J researchers.

Plant J is presently producing a-Si cells for research purposes. Three types of a-Si cells have been produced: Schottky barrier cells, metal-insulator-semiconductor (MIS) cells, and cells with an undoped a-Si insulating layer between P-doped and N-doped a-Si (P-I-N cells). Cell production involves metallization of substrate and deposition of cermet* film, a-Si layers with appropriate dopant, contact electrode, and antireflective coating.

Metallization

Glass substrates are made conductive by depositing a transparent layer of tin oxide (SnO_2) or indium tin oxide ($InSnO_2$) with vacuum evaporation or RF sputtering. In addition to transparent conductors, metallized glass substrates are used in fabricating cells. For some devices, stainless steel substrates are used, and metallization is not required.

Deposition of Cermet Film

In fabrication of the P-I-N cell, only a thin cermet film is evaporated onto the transparent conductive substrate. The cermet film is composed of platinum and silicon dioxide ($Pt-SiO_2$), has good electrical properties, and acts as a contact layer to the following p^+ layer of a-Si.

Deposition of a-Si and Dopants

The next step is the deposition of the a-Si layer. Deposition of the a-Si layer was by RF- or DC-induced glow discharge or sputter deposition. This was accomplished by pulling a vacuum on the system and bleeding in silane (SiH_4) at approximately 20 cm^3/min.

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*Cermet is an alloy of a heat resistant compound and metal.

Pressures from 10 to 300 millitorr are typical for this process. An RF or DC discharge is struck within the system, and a layer of hydrogenated amorphous silicon is formed on the heated substrate [300° to 350°C (570° to 660°F)]. The hydrogen content of these films may range from 10 to 50 percent. One deposition chamber uses a motor-driven shutter to vary the thickness of the layer and variable temperature controls to adjust substrate temperature.

The primary dopants used are diborane (B_2H_6) for boron doping (p-type) and phosphine (PH_3) for phosphorous doping (n-type); both gases are supplied in small gas cylinders. The amount of dopant added is electronically monitored in one deposition system and manually controlled in the other. Dopants are bled into the chamber with the silane. The amount of diborane introduced is 0.01 to 0.1 percent by volume of the discharge atmosphere. The phosphine added is about 0.2 percent by volume of the discharge atmosphere.

Deposition of silane and dopants is frequently performed in an argon atmosphere. Argon is also used to maintain a backpressure in the system and eliminate any moisture, because diborane and silane will combust spontaneously upon contact with moisture. All excess diborane, phosphine, and silane are vented to the atmosphere with the argon.

All roughing pumps and exhausts are located on the roof level, out of the working area. The process pumps are maintained with chlorofluorocarbon or fluoropolyether oils, which have extremely long lifetimes. Fiberglass filters are used on the inlet side of many systems to protect against colloidal silicon, which can cause pump failure. Canopy hoods are located above the deposition chambers to provide ventilation, and gas cylinders are located in enclosed exhaust hoods.

Plant J is experimenting with silicon tetrafluoride (SiF_4) for deposition of a-Si-F-H films to test recent claims that this material exhibits some advantages over Si-H films.

Deposition Of Contact Electrode

Contact electrodes are evaporated by vacuum onto the cell. For Schottky barrier and MIS cells, platinum (Pt) electrodes are deposited. For large cells a collection grid is required on top of the Pt layer. Grid electrode materials used for cells are typically titanium, aluminum, chromium, and copper.

Deposition of Antireflective Coating

An antireflective coating of either zirconium oxide (ZrO_2) or titanium oxide (TiO_2) is evaporated on the Schottky barrier cell as the final layer.

Waste Treatment and Handling

Waste is not a significant problem because operations are on such a small scale. Quantities of materials are very small and are used with a minimum of waste to keep cell costs low.

PROPOSED PRODUCTION PROCESS

Though a-Si cells are presently produced for research purposes on a batch-type basis, a "research system" allowing assembly-line production of a-Si cells is being designed and will be installed. This system is to be used for various research purposes and not solely for producing a-Si cells. The system will consist of up to four in-line deposition or etching stages, including glow discharge or sputter deposition chambers. With this system, deposition rates of 1 μm/min will be possible, and substrate size will be 0.1 m^2 (1 ft^2). The gas used in the plasma etch can be carbon tetrafluoride (CF_4). Because corrosive gases will be emitted from this process, a wet scrubber will be used to scrub the gases before discharge to the atmosphere. Deposition of the a-Si layer with silane will require about 10 minutes, whereas doping will require from 10 to 20 seconds. Process pumps will be located in a separate room adjacent to the processing area. Gas and chemical tanks will also be located in a separate room. The ventilation systems of both rooms will be separated. An argon atmosphere will be maintained in the deposition chambers to prevent formation of moisture.

Other operations in the proposed system may include plasma etching, laser or mechanical pattern scribing, ion implantation, and annealing. Annealing will be required to repair the cell, because ion implantation damages amorphous cells.

SURVEY OBSERVATIONS

All enclosures appeared to be adequately designed and constructed. Though some equipment items are ventilated by somewhat makeshift enclosures, they were considered adequate for the intended purpose of providing supplementary ventilation around a vacuum chamber. Toxic gases are stored in enclosures ventilated by bleed from ductwork running to standard laboratory hoods. Because some laboratory hoods are connected to exhaust fans on the roof, a maintenance shutdown of the fan is possible. It was stated, however, that laboratory personnel would be notified before a shutdown. Hoods and vented enclosures were reportedly checked annually by maintenance engineers trained by the Safety Officer.

CONCLUSIONS

In-depth assessment of operations is not necessary because the majority of operations are enclosed and well controlled, because only small amounts of chemicals and a few experienced technical personnel are involved, and because operations are on laboratory scale. Envisioning potential problems of the online process being constructed is difficult, but provisions for a safe work environment will apparently be adequate.

PLANT K: CADMIUM SULFIDE (CdS) R&D FACILITY--SAMPLING SURVEY

INTRODUCTION

Plant K was chosen for an in-depth survey because it appeared closer to commercialization of nonsilicon modules than other plants. A walk-through survey was conducted at this plant on October 31, 1978.

PLANT DESCRIPTION

Plant K, which is owned jointly by several companies, is involved solely in the commercialization of solar photovoltaic panels manufactured in a unique cadmium sulfide/copper sulfide (CdS/Cu_2S) process. The facility is a pilot plant and is contained in one building. Construction was started on this facility in April 1977.

DESCRIPTION OF WORK FORCE

Currently the plant has 25 nonunion production operators working week days on the day shift only. Women comprise 15 to 20 percent of this total. Most operators are under 25 years of age and relatively unskilled.

MEDICAL, HEALTH, AND SAFETY PROGRAMS

All new employees are given complete physical examinations including baseline blood cadmium and lead tests. Line personnel are then tested twice a year for cadmium; all other personnel are tested once a year.

Plant K does not employ an industrial hygienist; the plant manager serves as the safety and health supervisor.

DESCRIPTION OF PRODUCTION PROCESSES

The key to this process is the very low cost of the finished panels. The panels are large 40 by 61 cm (20 by 24 in.), and are expected to produce up to 10 watts, operating at 18 volts. Panel assembly consists of joining 8 panels in a module and 8 to 10 modules in an array that weighs about 450 Kg (1000 lb). The pilot pilot plant only can make 10 to 20 panels per day; however, the scaled-up commercial plant planned for startup in June 1980 will make 700 to 800 panels measuring 50 by 61 cm (24 by 24 in.). By late 1981 the company hopes to produce a panel costing less than 5 dollars per watt. A 5 percent conversion efficiency is also hoped for.

The low cost is possible because panel manufacture consists of little more than spraying a series of chemical layers onto hot glass moving on a continuous conveyer. The operation starts with sheet glass, either obtained precut or cut to size at the plant. The glass is cleaned with detergent and deionized water and then dried in stationary dryers. (The larger plant will use an automatic washer.) Cleaning and drying are important for producing an adherent surface. Two types of glass are used: standard float glass and low-iron glass, the latter allowing more light to pass through. One operator is involved in glass cutting and cleaning operations.

Cadmium Sulfide Application

After inspection, the glass is put on a trolley for transfer to an automatic horizontal conveyer, which carries glass through all the spraying operations. The glass first passes through a convective furnace where it is uniformly heated to between 400° and 500°C (750 and 920°F). Once out of the furnace, the glass is uniformly coated with a light spray of tin chloride in methyl alcohol. The solution is applied with a spray nozzle that traverses the glass as it moves steadily along the production line. The tin chloride oxidizes on contact with the glass, and the resulting exhaust is enclosed under a hood and ventilated. The static pressure within the spray chamber is monitored continuously and is adjusted when necessary with a manual fresh-air bleed downstream of the hood.

The remaining operations involve a series of CdS spray chambers. These are ventilated by enclosures similar to that used for the tin chloride spray; however, the enclosures do not allow for static pressure monitoring. There are a total of seven CdS spray chambers, one group of three and one group of four. The first group of sprays, containing dilute aqueous cadmium chloride and thiourea, form a CdS layer of about 2μm ($\leq$2μm) thickness. After they have been sprayed, the panels are moved to an open area where they are inspected. This operation is also enclosed. An operator slides panels by hand to a second battery of sprays of a similar CdS solution to obtain a total CdS thickness on the panels of about 5μm ($\leq$5μm). Following this spraying process, the CdS layers are then subjected to heat treatment. The panels are heated to 450° to 550°C (840 to 1020°F) in an enclosed convective heater. Three or four workers are involved in the operations on the coating line. Each is responsible for maintenance of a section of the line. Some operators were observed working on the spray equipment through an open door on the front of the chamber enclosure. Figure 1 is a sketch of the spray line layout.

Panel Subdivision

After the panels are removed from the spray line, they are transported in carts to a precision scraping operation. The grid pattern for the panel is formed by scraping lines across the panel down to the tin layer. Sixty lines are scraped sequentially. (In the larger plant this operation will be automated to produce six lines simultaneously, all indexed.) As the lines are scraped, a needle applies a strip of permanent resist while a second applies a removable strip. This operation is patented. Compressed air is blown on the panels to remove dust.

Panel Cleaning and Copper Chloride Application

Panels are taken on a holder through a series of baths to form the Cu_2S layer. The panel is mounted on a holder and sequentially dipped by a pulley system in:

1. a pre-edge solution of "mild" tartaric or citric acid
2. a deionized water rinse
3. an aqueous solution containing copper ions
4. a second deionized water rinse
5. a second aqueous solution containing a different concentration of copper ions
6. a final deionized water rinse

The copper chloride ($CuCl_2$) solutions also contain other compounds to help form the Cu_2S layer. The tanks are discharged by gravity every 1 to 2 days.

Evaporative Metal Coatings

The panels are then loaded into the vacuum evaporation chamber. This sealed cylindrical vessel on rollers holds two lots of four panels each. The evaporator operates at 6.7×10^{-4} Pa. Three metals in pellet form are sequentially evaporated in the chamber as it rotates. Then the chamber vacuum is broken, and the panels are removed and loaded into a slide oven. The oven operates at 150° to 300°C (300° to 570°F) and has a circulating air fan. Panels are removed from the oven and cooled, and the removable resistance strip is taken off. The panels are then finished and ready for electrical testing and mounting.

The panel mounting was not observed during the survey. Mounting is reportedly still very much in the development stage.

Pollution Control

Each spray operation is enclosed and emissions are ducted to three exhaust ventilation systems. There is one system for the tin chloride spray line and one system for each of the sets of CdS sprays. Each exhaust airstream is scrubbed in a separate countercurrent water scrubber, which is "homemade" and contains five trays. Air from the scrubbers is exhausted above the roof. Air samples from the CdS lines taken from the scrubbed air showed a 150 to 250 $\mu g/m^3$ cadmium concentration range. Wastewater from the scrubbers goes to two successive holding tanks. The first tank is baffled to settle solids, and the second is pH adjusted to precipitate cadmium. The discharged water has been found to contain 20 to 50 ppb of cadmium.

During warmer seasons, the building air exhaust rate from each of six fans is 3400 m^3/min (120,000 ft^3/min). Plant K has not found cadmium in plant air even during colder periods, when only a small amount of exhaust is emitted.

Of the cadmium sprayed in the operating line, about half sticks to the panels; the remainder is either exhausted in the process ventilation system or it adheres to the trolleys, booth, fans, or exhaust line surfaces. The scrubbers are estimated to recover 90 to 95 percent of cadmium: 4.5 Kg/yr (10 lb/yr) is exhausted to the atmosphere and about 70 Kg/yr (150 lb/yr) goes to the scrubber water for treatment.

Commercial Plant

The commercial size plant will be basically a scaled-up version of the pilot plant. The spray line will move at about six times the speed of the pilot and have 44 spray booths. About 900 Kg/yr (20,000 lb/yr) of $CdCl_2$ will be required.

SURVEY PROCEDURES

Air samples were collected to evaluate the exposure of workers to cadmium, thiourea, tin, and methyl alcohol in the spray line operation. Samples were also collected in the cell division area to measure cadmium and lead exposures. The major portion of the survey was devoted to evaluating time-weighted-average (TWA) exposures in the workers' breathing zones.

Samples were collected under normal operating conditions with different general building ventilation rates and also during cleanup of the apparatus used in the spray line and the metallization (cell division) processes.

The following are brief descriptions of the techniques used to collect and analyze the air samples obtained during the survey.

Cadmium

All cadmium air samples, both personal and area, were obtained by drawing air at a flow rate of about 2 liters per minute through standard closed-face millipore filter cassettes with Mine Safety Appliances Model G or Bendix BDX 55HD personal sampling pumps. For personal samples, pumps were attached to the worker's belt, and the sampling tubes were clipped in a vertical position to the lapel or shirt collar. Some filter cassettes were changed halfway through the shift whereas others, particularly those used for area samples, were left in place for a full shift. Some short-term peak exposure samples were collected, especially during cleanup operations.

In the PEDCo Environmental laboratory, samples were analyzed with NIOSH analytical method S313 for cadmium fume and dust. In this procedure, the filters containing the samples are wet-ashed with nitric acid to destroy the organic matrix; cadmium and its compounds are then solubilized in a hydrochloric acid solution maintained at a pH of 1. The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer. A hollow cathode lamp for cadmium is used to provide a characteristic cadmium line at 228.8 nm. The amount of cadmium absorbed is proportional to the cadmium concentration (1).

Tin

Some millipore-filter samples collected for cadmium analysis in the tin oxide spray area were also analyzed for tin. Samples were analyzed with NIOSH analytical method S183. This procedure is similar to that described for cadmium above.

Thiourea

Exposure to thiourea, which is used in the cadmium spray solutions, was tested by personal sampling in the cadmium spray line area. Personal air samples were collected on polyvinyl chloride (PVC) filters at about 2 liters per minute by the same method used to collect cadmium samples. In the laboratory the samples were analyzed with NIOSH analytical method P&CAM 281 for ethylene thiourea. In these procedures the filter is extracted with distilled water. Pentacyanoamine ferrate reagent is added to the extent to form a colored coordination complex. The absorbance of the solution is measured spectrophotometrically at 590 nm, and the concentration of thiourea is determined from a calibration curve. The pentacyanoamine ferrate reagent will complex with compounds containing the thione (C=S) moiety; this method, therefore, will detect all compounds containing this moiety.

Methyl Alcohol

Methyl alcohol, used in the tin oxide spray solution, was sampled during normal spray line operation. Personal air samples were collected by drawing air at a rate of about 100 cm^3/min through standard silica gel tubes with SKC low-volume pumps. The pump was attached to the worker's belt and the sampling tube was placed in a holder and clipped in a vertical position to the lapel or shirt collar. Collected samples were capped and kept in a freezer upon return to the laboratory.

In the laboratory, samples were analyzed using NIOSH analytical method S59. In this procedure, the silica gel in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with water. An aliquot of the desorbed sample is injected into a gas chromatograph. The area of the resulting peak is determined and compared with the areas obtained from the injection of standards.

Lead

Personal exposure to airborn lead was monitored in the cell division area. Lead was sampled by a method similar to that described for cadmium above.

Lead samples were analyzed in the laboratory with NIOSH analytical method S341. Samples are wet-ashed with nitric acid to destroy the organic matrix, and the lead is then solubilized in nitric acid. The solutions of samples and standards are analyzed by aspiration into the oxidizing air-acetylene flame of an air atomic absorption spectrophotometer with a hollow cathode lamp for lead.

Toluene

A personal sample was collected for toluene in the cell division area.

The toluene sample was analyzed in the laboratory with NIOSH analytical method S343. In this method, the charcoal sample in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide. An aliquot of the desorbed sample is injected into a gas chromatograph. The area of the resulting peak is determined and compared with areas obtained from standards.

RESULTS AND DISCUSSION

Tables K-1 to K-5 present the results of sampling for cadmium in the spray line area during normal operation and during cleanup operations, and for tin, thiourea, and methyl alcohol. Tables K-6 and K-7 present results of sampling in the cell division area for cadmium and lead. Table K-8 presents the results of other sample analyses. When samples were changed on a worker during the shift, TWA exposure was calculated. The sampling results are summarized in Table K-9.

The building uses three seasonal ventilation modes: in winter, little general ventilation; during spring and fall, the use of exhaust fans behind the spray line; in summer, the use of exhaust fans and fans to cool makeup air. On March 13, 1979, the summer ventilation mode was used. On March 14, 1979, no local ventilation was used in the morning (0800 to 1200 hours); all exhaust fans were used in the afternoon (1200 to 1700 hours). On March 15, 1979, two exhaust fans were used in the morning and all four fans were used in the afternoon.

Spray Line--Cadmium

Tables 1 and 2 present the individual personal sample results and estimated TWA exposures as well as the area sample results for airborne cadmium levels in the spray line area.

Table 1 is based on samples collected under normal operating conditions. Results show exposures for spray line operators, for the area supervisor, and area samples. Exposures for spray line operators ranged from 13.8 to 29.8 $\mu g/m^3$. The highest measured operator exposure was 59.3 $\mu g/m^3$ for a short-term (2 h) sample taken from an operator working throughout the line. No specific cadmium exposures were identified that would cause this elevated exposure. Two personal samples were collected on the area supervisor. The first sample, collected on March 13, 1979, resulted in a 9.8 $\mu g/m^3$ exposure; the second sample, collected on March 15, 1979, showed 58.5 $\mu g/m^3$ exposure. The cause of the elevated level found in the second sample is not known. It was anticipated that the supervisor would show the lowest exposure because he spent much of the day away from the spray line. In fact, both of the high cadmium exposures were for workers doing nonroutine operator tasks.

TABLE K-1. CADMIUM EXPOSURE AT SPRAY LINE DURING NORMAL OPERATION

Date	Sample No.	Sample description	Time		Sample volume, liters	Total sample weight, µg	Concentration	
			Start	Stop			Cadmium $\mu g/m^3$	Estimated TWA $\mu g/m^3$
3/13	2	CdS No. 1 Spray operator	12:48	16:45	402	6.6	16.4	
3/13	3	CdS No. 2 Spray operator	11:25	16:40	536	15.1	28.2	
3/13	1	Tin Oxide Spray Operator	11:22 13:55	13:02 16:10	403	12.4	29.8	
3/13	4	Area sampling--between CdS No. 1 and No. 2 Spray lines	11:36	16:42	482	6.2	12.9	
3/13	7	Supervisor (throughout plant)	12:47	16:38	396	3.9	9.8	
3/15	31	CdS No. 1 Spray operator	8:48	12:58	426	5.9	13.8	
3/15	34	CdS No. 2 Spray operator	8:35 15:12	13:47 16:22	680	16.9	24.9	
3/15	30	Tin Oxide Spray operator	8:32 13:45	12:30 16:22	588	11.1	18.9	
3/15	33	Operator (throughout spray line)	8:40	10:53	226	13.4	59.3	
3/15	37	Area Sample--Spray area about glass dumpster	8:43	16:15	753	6.8	9.0	
3/15	29	Supervisor (throughout plant)	8:33	11:28	301	17.6	58.5	

TABLE K-2. CADMIUM EXPOSURE AT SPRAY LINE DURING CLEANING

Date	Sample No.	Sample description	Time		Sample volume, liters	Total sample weight, μg	Concentration	
			Start	Stop			Cadmium μg/m³	Estimated TWA μg/m³
3/14	10	CdS No. 2 spray operator clean up	8:38 10:15	9:14 12:00	243	4.3	17.7	
3/14	27	Operator (for Sample 10), cleanup	13:15	16:47	358	5.6	15.6	16.4
3/14	22	Tin oxide spray operator cleanup	9:53	12:04	201	9.1	45.3	
3/14	28	Operator (for Sample 22), cleanup on CdS No. 2	13:18	16:47	347	11.9	34.5	38.5
3/14	11	Tin oxide spray operator cleanup	8:38	10:06	152	7.4	48.7	
3/14	19	Operator (for Sample 11), CdS No. 2 cleanup	10:06	12:00	170	2.7	15.9	
3/14	26	Operator (for Sample 11), tin oxide cleanup, Cd_2S No. 1 spray operation	13:15	16:46	360	4.3	11.9	21.4
3/14	12	Operator for solution preparation and CdS No. 1 spray setup	8:42	9:56	128	1.4	10.9	
3/14	20	Operator (for Sample 12), Cd_2S No. 2 cleanup	9:56	12:00	201	165	821	506
3/14	13	CdS No. 1 spray operator, normal operation	8:47	11:12	248	2.6	10.5	
3/14	23	Operator (for Sample 13), normal operation	12:15	16:46	533	9.8	18.4	15.9
3/14	17	Supervisor--throughout plant	9:06	11:11	212	1.7	8.0	
3/14	24	Supervisor--throughout plant	12:15	16:47	469	2.1	4.4	5.5

TABLE K-3. TIN EXPOSURE AT SPRAY LINE

Date	Sample No.	Sample description	Time		Sample volume, liters	Total sample weight, μg	Concentration	
			Start	Stop			Tin, $\mu g/m^3$	Estimated TWA $\mu g/m^3$
3/13	1	Tin oxide spray operator, normal operation	11:22 13:55	13:02 16:10	403	2.2	5.5	
3/13	7	Supervisor--throughout plant	12:47	16:38	396	0.2	0.5	
3/15	30	Tin oxide spray operator, normal operation	8:32 13:45	12:30 16:22	588	11.6	19.7	
3/14	11	Tin oxide spray operator, cleanup	8:38	10:06	152	4.4	28.9	
3/14	26	Operator (for Sample 11), cleanup of Tin Oxide at Cd_2S No. 1 Spray line	13:15	16:46	360	0.2	0.6	0.9
3/14	22	Tin oxide spray operator, cleanup	9:53	12:04	201	9.1	45.3	

TABLE K-4. THIOUREA AT SPRAY LINE

Date	Sample No.	Sample description	Time		Sample volume, liters	Total sample weight, μg	Concentration	
			Start	Stop			Thiourea, μg/m³	Estimated TWA μg/m³
3/13	14	Operator preparation of CdS No. 1 spray solution	8:52	10:01	119	5.3	44.5	
3/13	21	Operator (for Sample 14), CdS No. 2 cleanup	10:01	12:00	202	4.6	22.8	30.8
3/13	15	CdS No. 1 spray operator, normal operation	8:55	11:12	241	5.1	21.2	
3/14	25	Operator (for Sample 5), normal operation	12:15	16:50	485	10.0	20.6	20.8
3/15	36	CdS No. 1 spray operator, normal operation	8:38	16:25	761	2.3	3.0	

TABLE K-5. METHYL ALCOHOL EXPOSURE AT SPRAY LINE

Date	Sample No.	Sample description	Time		Sample volume (liters)	Total weight (μg)	Concentration	
			Start	Stop			Space, mg/m^3	Estimated TW, μg/m^3
3/13	9	Tin oxide spray operator	13:08	16:10	12.7	40.8	3.21 mg/m^3 (2.5 ppm)	
3/15	35	Tin oxide spray operator	8:35 13;20	12:31 16;22	293	354.4	12.10 mg/m^3 (9.3 ppm)	

TABLE K-6. CADMIUM EXPOSURE IN CELL DIVISION AREA

Date	Sample No.	Sample description	Time		Sample volume, liters	Total sample weight, µg	Concentration	
			Start	Stop			Cadmium, µg/m^3	Estimated TWA µg/m^3
3/13	5	Cell division operator, primarily cleanup operations	12:52	16:13	312	20.5	65.7	
3/14	16	Cell division operator, cell division and cleanup	8:52	16:45	764	4.3	5.6	
3/13	6	Area sample--outside workshop 18 in. from discharge of vacuum blower from cell division area	11:52	16:15	459	4.5	9.8	
3/14	18	Area sample--same area as Sample 6	9:46	14:52	493	7.3	14.8	

TABLE K-7. LEAD EXPOSURE IN CELL DIVISION AREA

Date	Sample No.	Sample description	Time		Sample volume, liters	Total sample weight, µg	Concentration	
			Start	Stop			Lead µg/m^3	Estimated TWA µg/m^3
3/15	32	Cell division operator, preparation of lead bullets	8:40	11:37	310	5.3	17.1	
3/15	41	Same as sample 32	12:50	3:30	262	1.3	5.0	11.5

TABLE K-8. OTHER SAMPLES COLLECTED

Date	Sample No.	Sample description	Time Start	Time Stop	Sample volume, liters	Total sample weight, µg	Concentration µg/m^3	Concentration Estimated TWA µg/m^3
3/15	39	Cell division operator, cleaning permanent resist lines (toluene)	13:06	13:25	4.9	109	2.2 mg/m^3[a]	
3/15	40	Chemist in spray line area and on roof sampling Cd from exhaust (cadmium)	8:58	15:58	718	19.3	25.9	
3/15	38	Area sample--on roof 6 ft. downwind from exhaust vents of Cd_2S spray lines No. 1 and No. 2 (cadmium)	9:40	15:56	624	50.0	80.1	

[a] 0.6 ppm

TABLE K-9. SAMPLING SUMMARY

Location or job title	Pollutant	No. of TWA determinations	Range, $\mu g/m^3$	Mean, $\mu g/m^3$	No. of short-term samples	Short-term peak, $\mu g/m^3$
SnO_2 spray line						
Normal operation	Cd	2	18.9-29.8	24.3	0	
Cleaning	Cd				2	48.7
CdS_2 spray line						
Normal operation	Cd	2	9.0-24.9	17.0	7	59.3 (Mean 27)
Cleaning	Cd	4	5.5-38.5	19.1	3	821
SnO_2 spray line						
Normal operation	Sn	1	19.7		1	5.5
Cleaning	Sn	0			3	45.3
CdS_2 spray line	Thiourea	2	3.0-20.8	11.9	3	44.5
Cell division	Cd	1	5.6		3	65.7
Metallization preparation	Pb	1	11.5		0	

Two other area samples showed 12.9 and 9.0 μg/m^3 cadmium levels. The first sample was obtained from between the Cd_2S spray lines at 4 feet from the floor. The second sample was obtained from over the broken glass dumpster about 12 feet from the spray line (see Figure 1). The location of the first area sample is near the normal work area of the Cd_2S No. 1 spray operator. Two samples taken from this operator showed 13.8 and 16.4 μg/m^3 exposure. The area sample concentration closely agrees with these results. The Cd_2S No. 2 spray operator showed higher exposure levels of 28.2 and 24.9 μg/m^3. These elevated levels may result from the greater amount of cadmium being sprayed in the No. 2 line. Also, an exhaust vent is located closer to the No. 1 line. The cadmium exposures for the tin oxide spray operator were 29.8 and 18.9 μg/m^3.

Table 2 presents cadmium exposure data for March 14, 1979 during the spray line cleanup. About 4 h per week (or 8 h every 2 weeks) is devoted to disassembling the spray chambers and cleaning them. The tin oxide spray line cleaning was completed in the morning, and the operators of that line then assisted the Cd_2S No. 2 spray operator in cleanup of the Cd_2S No. 2 spray chamber for the remainder of the day. The Cd_2S No. 1 spray unit operated normally. The personal sample of the Cd_2S No. 1 spray operator showed a TWA exposure of 15.9 μg/m^3, which was consistent with area sample data presented in Table 1 for this job. The operator exposure measured during cleanup showed the highest levels. One sample (No. 20) showed exposure to a very high concentration, 821 μg/m^3 for a 2-h period. The operator from whom the sample was taken was vacuuming inside the Cd_2S No. 2 spray chamber for part of this time period. He was wearing a disposable face mask while vacuuming. Other than this high exposure, TWA exposures for workers on cleanup ranged from 16.4 to 38.5 μg/m^3, with a peak 2-h sample of 45.3 μg/m^3. The TWA exposure of the area supervisor during cleanup was 5.5 μg/m^3, which was lower than his exposures of 9.8 and 58.5 μg/m^3 for the other 2 sampling days.

No effect of different general ventilation modes could be detected from the sampling data. During cleanup (March 14, 1979) the winter ventilation mode was used. This mode should result in the highest exposure levels. Makeup and exhaust ventilation should reduce some of the elevated levels.

Spray Line--Tin

Table 3 presents the results of personal sampling for tin exposure on the spray line. Most of the tin should be in the form of tin oxide (SnO_2), which has a nuisance particulate TLV of 10 mg/m^3 The tin oxide spray operator had full-shift exposures of 5.5 and 19.7 μg/m^3 during normal spray line operation and 45.3 and 9.0 μg/m^3 during cleanup. Thus tin exposure is not of industrial hygiene concern.

Spray Line--Thiourea

Table 4 presents the results of personal sampling for thiourea exposure on the spray line. During normal operation, full shift exposures were 3.0 and 20.8 μg/m^3 on Cd_2S No. 1 spray line. During spray line cleanup the TWA exposure reported was 30.8 μg/m^3. This latter exposure included a 1-h peak exposure of 44.5 μg/m^3 during preparation of the Cd_2S spray solution, which contains thiourea. The instability of thiourea at spray line heater temperatures may help limit worker exposure.

Spray Line--Methyl Alcohol

Table 5 presents the results of personal sampling for the exposure of spray line operators to methyl alcohol. The two workers monitored showed 2.5 and 9.3 ppm exposures under normal operating conditions. Since the TLV for methyl alcohol is 200 ppm, these levels are not of concern in industrial hygiene.

Cell Division (Metallization)

Tables 6 and 7 present data on cadmium and lead samples collected in the cell division work area. During the survey, cell division was operated only on March 14, 1979, and resulted in a full-shift personal exposure to cadmium of 5.6 μg/m^3. During March 13, 1979, the cell division machine was cleaned and personal exposure levels rose to 65.7 μg/m^3, 12 times higher than that of normal operation. Airborne cadmium samples were also collected near the discharge of the ventilation vacuum blower for the cell division machine. The discharge was located just outside the building in a small workshop. During cell division operation (March 14, 1979) the cadmium concentration in the cell division area was 14.8 μg/m^3, during cleanup of the cell division machine the level was 9.8 μg/m^3.

In both the spray line and cell division areas, highest cadmium exposures are experienced during cleanup operations.

Personal samples were also collected on the cell division operator during preparation of lead bullets for vacuum metallization. This task involves cutting lead sheet, melting the lead, and pouring it into bullets. The TWA exposure was 11.5 μg/m^3, the average includes a higher morning level of 17.1 μg/m^3. The fact that most of the bullet forming was done in the morning probably accounts for the higher morning exposure. The TWA level is less than 10 percent of the TLV and thus is not significant.

A short-term personal sample was collected for exposure to toluene during solvent cleaning of the permanent resist lines in the cell division. The results presented on Table 8 show a 10.2 ppm exposure. This level of exposure is not a health concern.

Miscellaneous Samples

Table 8 presents results of area sampling for cadmium at a location 2 m (6 ft) downwind from the Cd_2S spray discharge lines on the building roof. The concentration measured was 80.1 $\mu g/m^3$. A personal sample was also collected from one of the plant chemists responsible for air sampling. His shift exposure to cadmium was 26.9 $\mu g/m^3$. This chemist set up and maintained a sampling train on the roof in the morning and worked near the spray lines most of the remainder of the day. His exposure was higher than that of personnel working in the cadmium area, as reported in Table 1, and higher than most of the exposure data for spray line operators. A higher concentration of cadmium on the roof is probably the cause of this higher exposure.

Ultraviolet Radiation

A single, small electric arc was used in the cell subdivision process. This operation involved one worker who, by close observation of the process, was exposed to a potential health hazard from ultraviolet radiation.

Although the severity of this hazard was undetermined, it would be advisable to provide shielding for the ultraviolet source to protect the operator and others working in the area. It would also provide additional protection for the potential physical hazard of material splatter, although this is not considered a serious problem in electric arc use.

Shielding should be possible without causing interference with the operation and monitoring of the subdivision process. Appropriate safety glasses could serve as interim or supplementary protection.

Further reason for shielding is that the use of "second generation" equipment may involve the simultaneous striking of several arcs. This would compound the potential hazard of the single-arc unit.

Spray Chamber Ventilation

Local exhaust ventilation has been provided for process operations involving: 1) tin oxide spray coating, 2) cadmium sulfide spray coating, and 3) cell subdivision. General forced exhaust and supply ventilation also exists, with three (seasonal) primary modes of operation.

Local exhaust hoods on the tin and cadmium spray operations were found to be adequate for contaminant control. Contaminant may be released, however, if access doors are left open during spray operations. Each cycle of the spray nozzle sprays very near to the access opening. A wider enclosure may be advantageous.

Inlet velocities during normal operation with access doors closed were about 56 m/min (170 ft/min) average at the primary air inlets and about 66 m/min (200 ft/min) at the bleed air inlets. Face velocities at access openings to the spray chambers averaged 50 m/min (150 ft/min) from the larger, sliding doors, and 56 m/min (170 ft/min) from the smaller, hinged doors.

These velocities were considered adequate for ventilation. The general performance and design of these ventilation controls were appropriate and effective.

Cell Subdivision Ventilation

Local exhaust ventilation was provided for the cell subdivision process. Cadmium sulfide dust was collected by a vacuum cleaning system through a small nozzle positioned near the point of contaminant release. The cleanliness maintained on the cell surface during the subdivision process indicated that collection was efficient.

The vacuum cleaning system consisted of a small wall-mounted exhauster/filter unit in a small room with a door opening to the outside. This room was used occasionally as a supplementary shop area.

Area air samples were taken at a drill press stand near the discharge point of the vacuum cleaning system. The sample data should indicate a minimum health hazard potential in this area.

Plans for acceleration of the subdivision process should take into account any additional problems that might result.

General Plant Ventilation

General plant ventilation consisted of six roof-mounted supply air and air conditioning units. Plant air was exhausted through four wall-mounted exhaust fans along the primary process line. Air was also exhausted from the several laboratory areas through the laboratory exhaust hoods.

The system operated under three basic operational modes: 1) spring: wall exhaust on, supply off, doors open, 2) summer: wall fans on, air supply/conditioning on, doors closed, and 3) winter: wall exhaust on/off, air supply off, space heaters on. Air samples were taken during typical operations, and are expected to show safe levels for each general ventilation mode.

Supply air was provided through diffusers directly overhead in the process area. Two units were located such that the process line was at about midway to the wall exhaust fans. This arrangement provided adequate general air flow and fresh air exchange.

Air also may be supplied to office, laboratory, shop, storage, and other areas by overhead ducting from four of the air conditioning units. Aisles, open doors, and "loose" construction of the plant interior rooms facilitated general airflow through these areas. General ventilation was adequate.

CONCLUSIONS

The following conclusions are based on the results of sampling data and observations made during the walk-through survey.

(1) During normal operation of the spray line, most TWA personal exposures to cadmium were below 30 $\mu g/m^3$. The current TLV for cadmium is 50 $\mu g/m^3$ and the OSHA standard for cadmium fumes of 100 $\mu g/m^3$. No personal sample for the normal spray line operators exceeded 30 $\mu g/m^3$. Area samples showed low cadmium levels. The two elevated exposures (59.3 and 58.5 $\mu g/m^3$) could not be explained on the basis of job functions. One of the samples was for the supervisor (58.5 $\mu g/m^3$), who had the lowest exposure (9.8 $\mu g/m^3$) on the previous day of normal operation.

Because spray chamber ventilation and local ventilation appeared adequate, elevated exposures are probably due either to sample contamination or to reentrainment of cadmium dust.

(2) Care should be exercised to avoid allowing the ingestion of cadmium by workers. Operators at times handled glass racks and other cadmium-contaminated equipment with bare hands. Moreover, clothes contaminated with cadmium are often worn home. At a production level, operators should change clothes at work.

(3) During cleanup of the spray line, some elevated cadmium exposures resulted. The only exposure above 50 $\mu g/m^3$ was from a 2-h sample showing 821 $\mu g/m^3$ exposure. This was the dirtiest operation and the only one for which a face mask was worn. The operator from whom the sample was obtained was running a vacuum cleaner on CdS spray line surfaces, which probably resulted in the carrying of cadmium to nearby surfaces. Because containment of cadmium is essential, such vacuuming is not an adequate cleaning procedure. For such a high exposure level, a disposable face mask cannot be considered adequate. Until cadmium exposure is reduced, it is recommended that a fitted mask with air purifying cartridge be used.

Cleanup of the tin oxide spray system resulted in elevated cadmium exposures of 45.3 μg/m^3 (Sample 22) and 48.7 μg/m^3 (Sample 11). This appeared to be an unusually thorough cleanup, necessitated by solids buildup on chamber walls.

(4) Care should be exercised during cleanup of the spray chambers and spray chamber vent ducts to prevent excessive worker exposure to the cadmium likely to build up there. Personal exposure measurements should be made.

Care should also be exercised in handling the waste sludge and cleaning the settling tanks. These are potentially significant cadmium exposure sources.

(5) Neither tin oxide nor methyl alcohol exposures appear to present significant health hazards. Levels found are well below 10 percent of their respective TLV's.

(6) The exposure of CdS spray operators to thiourea was comparable in level to their exposures to cadmium. No TLV exists for thiourea; however, it is known to be quite toxic. Reduction in exposure of spray line operators to cadmium should simultaneously reduce thiourea exposures. The first thiourea exposure found was in CdS spray solution preparation (44.5 μg/m^3). This operation takes only 1 to 1-1/2 hours per day and at this exposure level is not considered a significant exposure.

(7) In the cell division operation, only unit cleanup resulted in elevated cadmium exposure (65.7 μg/m^3). Improved cleanup practices and improved ventilation are recommended.

(8) Local exhaust systems are believed to provide adequate control. Air supply systems were sufficient to provide makeup air and air cooling. General ventilation was used primarily to provide temperature control, and secondarily to supplement air contaminant control.

(9) Ultraviolet radiation during cell subdivision was a potential hazard.

(10) The work areas were generally well controlled, particularly for a pilot line operation. A scaled-up production facility will probably have more complete enclosure and more continuous operation. These factors should reduce workplace exposure because the highest exposures appear to be related to cleanup operations.

Current ventilation techniques appear to be quite adequate.

RECOMMENDATIONS

Cleanup procedures should be reviewed to reduce cadmium exposures and release of cadmium into the room area. These problems were most evident during the vacuum cleaning of the CdS spray chamber areas. Although the worker doing the cleaning was wearing a disposable face mask, he was probably still exposed to cadmium in excess of the TLV. Possible alternatives are an improved vacuum system or wet cleaning methods. It is recommended that exhaust vents be on at all times during cleanup.

Shielding of the ultraviolet radiation from cell division should be studied, particularly if a scaled-up cell division machine is to be used in the larger plant.

PLANT L: CADMIUM SULFIDE (CdS) R&D FACILITY WALK-THROUGH SURVEY

SUMMARY OF SURVEY FINDINGS

Plant L is developing a front-wall photovoltaic solar panel using cadmium sulfide and copper sulfide (CdS and Cu_xS). Vacuum evaporation of CdS on prepared panel substrates appears to be the process of most concern from an industrial hygiene viewpoint. No significant industrial hygiene problems were observed; however, most process steps were at bench-top scale or were being changed frequently, thereby making characterization of industrial hygiene difficult.

PLANT DESCRIPTION

Plant L is a subsidiary of a major oil company, which owns 80 percent of its stock. Founded in 1973, the plant is located in one contiguous building with an area of 33,000 ft^2 in the Eastern United States. All production-process development work at the plant is involved with CdS/Cu_xS photovoltaic panel production.

DESCRIPTION OF WORK FORCE

About 25 nonunion operators, of whom 85 to 90 percent are women, work during the day shift for 5 days a week. A turnover rate of 20 percent per year was reported.

MEDICAL, HEALTH, AND SAFETY PROGRAM

All new employees are required to provide a work history and to take a medical examination. Periodic medical tests are run on workers in certain areas, including the CdS evaporation area where blood serum cadmium levels are monitored semiannually. No job-related lost-time accidents were reported in 1978.

Plant L has hired an industrial hygienist consultant from the parent company. The CdS evaporator operator is monitored monthly for CdS exposure over three evaporator operating cycles. The facility maintains a formal safety program.

PROCESS DESCRIPTION

The Cu_2S-CdS front-wall photovoltaic solar cells being developed by Plant L consist of the following layers:

Front cover glass
Adhesive compound
Front contact grid
  Cu_xS: P Layer
  CdS: N Layer
Back contact
Steel substrate

The assembly is sealed in a metal pan with terminal connections.

Base Preparation

Plant L buys rolled steel, which is cut into approximately 8-inch squares to serve as the substrate. The steel substrate on the leaf holders is cleaned in a degreasing bath containing Freon. The degreaser is located in the main process area.

The substrate is further prepared for the back contact and thin bonding layer applications. The substrate in the holders is sequentially dipped in an alkali cleaner, a dilute sulfuric acid solution, and the back contact solution; it is then spray rinsed.

CdS Evaporation

A large horizontal batch vacuum evaporator is used to evaporate CdS under controlled temperature and pressure conditions to produce the desired crystalline CdS coating on the steel plates. This batch operation is located in a separate room. The operating cycle takes several hours and includes loading the substrate (which is in individual holders), closing the vessel end flange, pulling a vacuum, operating heating and cooling cycles, evaporating the CdS power in crucibles, and releasing the vacuum. A roughing vacuum oil-sealed pump located adjacent to the evaporator is vented to the outside. The vessel is equipped with cryogenic shields to reduce CdS vapor leaving the container.

The CdS gradually builds up on the evaporator inner walls and is removed periodically. Maintenance personnel chip off the CdS, which builds up as flaky, layered, crystalline deposits; the personnel then vacuum the inner vessel surface. Workers wear respirators during this operation. The waste CdS is disposed of by a contractor. Only high-purity CdS can be used.

Plant L is designing a semicontinuous evaporator equipped with air locks to prevent exposure of the hot chamber. This evaporator will be able to operate without opening. Plant L plans to recover the CdS removed from the evaporator inner walls.

One operator is stationed in this area, and a quality control technician works inside the vessel periodically. The exposure of the operator to CdS dust is monitored monthly by personal samples collected during three evaporation cycles of several hours each. The exposure levels ranged from 2 to 14 $\mu g/m^3$.

Base Preparation and $CuCl_2$ Dipping

Portions of the substrate are then coated with an impervious compound prior to Cu_xS layer application. This operation is performed piecemeal under a small hood.

The substrate is then dipped in a series of baths to form the Cu_xS layer. Held on a carrier, the material is wet etched in a strong acid solution, then dipped in a rinse bath and a vat of hot dilute copper salt. The acid batch is connected with a side exhaust vent and the copper salt bath is equipped with a slot side-draw hood. This system was not operating during the walk-through.

The used acid solution is reportedly drained directly to the sewer at the end of each day's operation.

The contact grids, which consist of copper, nickel, and gold layers, are applied sequentially by a proprietary process and then laminated. The area is ventilated in each application stage.

Module Assembly

The CdS/Cu_xS module is encapsulated in a metal pan with a glass front that is hermetically sealed to exclude oxygen and moisture.

The pans, which are purchased prefabricated, are first degreased in a tank that holds trichloroethylene and is equipped with chiller coils. The pans are then manually pretinned.

A standard low-temperature solder is used to interconnect the array. The connection pattern depends on the module output characteristics desired. The epoxy used in the process is cured in a vented oven. These operations are performed in a bench-scale hood.

The tempered glass faceplate is then sealed with solder to the pan assembly, and the seal is tested for leaks.

A clear fluid is pumped into the module air space behind the glass plate through pan openings. Terminals are then soldered in place on the pan back covers, and the surface of the pan is painted for improved appearance.

Finally, the modules are assembled into modular panels and interconnected for power transmission. Panel tests were observed at the facility; both operations take place in natural sunlight, and the accelerated tests are performed under artificial light.

SURVEY OBSERVATIONS

Many process operations are on a small batch scale operated on an intermittent basis, thus limiting the value of an industrial hygiene review.

Base Preparation

The steel substrate cleaning and coating baths are on a small scale. Two side-draw vents with a common duct are used on the H_2SO_4 bath.

Cd Evaporation

Potential sources of CdS exposure appear to be from handling and weighing CdS prior to evaporation, from the release of CdS dust or contact with CdS-coated surfaces during unloading and loading of substrate in the evaporator, from CdS leaks from the vacuum pump, and from exposure during removal of the CdS coating from the evaporator inner walls. The last operation appears to have the highest exposure potential; even with a continuously operating evaporator, this maintenance operation would be required periodically.

The evaporator area uses a separate air intake and vent. Some ceiling tiles were removed, which increases the likelihood that other building areas will be contaminated.

Base Preparation and $CuCl_2$ Dipping

The Cu_xS plating process operations were not running during the walk-through. No significant potential industrial hygiene problems were observed.

The contact grid application procedure appeared well ventilated with side-draw and canopy hooding. No health or safety problems were observed.

Module Assembly

Ventilation design for the module pan trichloroethylene degreaser appeared adequate.

Although the process steps involved the most labor, many of them would probably be automated if production were substantially increased. Solder used for interconnecting, and front-glass seal and epoxy used to bond the array in the pan, appeared to be the most significant problems from an industrial hygiene viewpoint. Hooding was provided for the soldering operations. The module glass front was cleaned with cloths dampened with isopropyl alcohol. Because these operations were conducted at bench-scale level, worker exposures were more difficult to characterize than they would be on a production line in which functional work areas are more clearly defined.

COMMENTS

Although no significant industrial hygiene problems were observed, many of the operations could not be adequately characterized. Among the reasons were the proprietary nature of a particular process, the operations not being performed during the walk-through, and the bench-scale level of many of the operations. Overall consideration should be given to the following issues related to industrial hygiene:

> The CdS evaporation vacuum pump should be located in a separate room and should be vented to the atmosphere.
>
> Maintenance workers removing CdS buildup from the evaporator inner wall should be monitored for air exposure to CdS dust.
>
> The base-plate Freon degreaser should have local ventilation (even though Freon is relatively nontoxic), in conjunction with good design practice.
>
> The ventilation should be checked in the module assembly where the soldering operations occur. This may not currently pose a problem because of the low production levels.

PLANT M: GALLIUM ARSENIDE R&D FACILITY--WALK-THROUGH SURVEY

SUMMARY OF SURVEY FINDINGS

The Plant M facility is the site of basic research and development work on single-crystal gallium arsenide (GaAs) photovoltaic cells starting with GaAs wafer material. Work is conducted on a small laboratory scale under controlled conditions. The use of well-trained scientists and technicians reduces the likelihood of industrial hygiene problems. All toxic materials appear to be adequately contained.

PLANT DESCRIPTION

The photovoltaic research is conducted within the larger III-V materials group of this large multifaceted research center. Most of the photovoltaic work is conducted in two laboratory rooms.

DESCRIPTION OF WORK FORCE

Well-trained scientists and technicians conduct the research. Technicians are nonunion.

MEDICAL, HEALTH, AND SAFETY PROGRAM

The R&D facility uses a medical clinic for emergency medical care and has a full-time nurse on staff.

Employees are given a medical examination when they are hired; they are given an annual or semiannual examination thereafter, depending on which chemicals are used in their work area.

The facility has a safety and industrial hygiene officer. No routine industrial hygiene measurements are taken; however, one survey has been conducted for airborne arsenic.

DESCRIPTION OF PHOTOVOLTAIC PROCESSES

Although Plant M is producing a demonstration GaAs concentrator array, the cell production processes are primarily focused on research. Purchased GaAs wafers are the starting material.

Wafer Preparation

Plant M first cleans the wafers in solvents in the following order: trichloroethylene, acetone, methyl alcohol, and isopropyl alcohol (to dry). Each solvent is used to remove different organic residues. The wafers are placed in a holder and dipped in turn into each beaker of solvent. The operation is enclosed under a laboratory hood.

Wafers are then individually etched in a solution of sulfuric acid and hydrogen peroxide, rinsed with water, and dried with isopropyl alcohol.

Liquid Epitaxial Growth

Layers of GaAs and GaAlAs are added to the GaAs starting substrate surface by liquid phase epitaxial growth (LPE). Preweighed source materials (Al, Ga, GaAs) are added to a multicompartment boat in a closed quartz tube, vented at one end. The quartz tube is initially pumped with a carbon vane pump and then a cryogenic sorption pump. The tube is then back filled with high purity H_2 gas and is subsequently maintained with a continuous H_2 flow of 250 cc/min. The quartz tube is guided part way into a cylindrical Marshall furnace, far enough to heat a multicompartment boat. The metal melt is allowed to equilibrate and then the melt is positioned over the substrate and the furnace temperature is lowered to form the required GaAs and GaAlAs layers. After growth, the wafers are ready for cell processing. The LPE melts contain $\sim$99 percent Ga and are recycled by the Ga supplier to recover the Ga.

Metallization and Antireflective Coatings

Cell fabrication consists of defining the cell area on the wafer and applying an ohmic metallization and an antireflective coating. Wafers are first rinsed in a sequence of beakers containing trichloroethylene, isopropyl alcohol, and acetone. This process is done manually under a laboratory hood. Wafers are next etched with bromine solution (also under a laboratory hood). A photoresist pattern is formed on the wafer by spinning on a photoactive material with a photodeveloper. The mask is positioned on the wafer with a microscope aligner.

Metallization layers are formed in vacuum bell jars. The top-side ohmic contacts include zinc, silver, and manganese. Layers of silver and germanium are applied to the back surface to form ohmic contact.

Wafers are mounted on holding plates in the bell jars, which contain 6 evaporation positions to evaporate metal in carbon crucibles with an electron beam. The vacuum pumps for the bell jars are located on the lower floor of the building.

The inner surfaces of the bell jar are cleaned periodically with a hand vacuum and by blowing with nitrogen. This operation is performed to prevent flaking of the metal from the jar surface.

The photoresist mask is removed by dipping the wafers in acetone under a laboratory hood. The thickness of the top-side ohmic contact metallization is then built up by electrochemical plating. The wafers are mounted on a metal substrate and dipped into a silver cyanide plating solution. The plating process is conducted under a laboratory hood.

Antireflective coatings of tantalum pentoxide and silicon dioxide are vacuum evaporated on the wafer to reduce losses in the cell and provide an encapsulation.

Future Expansion

The company will acquire the capability to grow its own gallium arsenide ingots and to slice wafers. An Czochralski puller has been purchased that is capable of producing a 7.5-cm (3-in.) diameter ingot weighing up to 5 kg (12 lb) each. The largest ingot currently available on the market is 3.25 cm^2 (1.25 $in.^2$). The puller will operate at 200 to 500 psi and 1230°C (2245°F) with a boric oxide cover layer over the GaAs melt to prevent arsenic loss. An inert (Ar) blanketing gas will also be used in the chamber.

A gauge will be used to saw wafers. The saw will be hooded to contain metal dust emissions.

Module Development

The company has a demonstration project with another firm to design and build a 256-cell GaAs dense array. In this design, the modules are tightly packed for large area, highly concentrated sunlight. The dense array is designed for operation at concentrations up to 1500 suns and temperatures of 180°C (356°F). An overall efficiency of 16 percent is anticipated, with individual cells exceeding 20 percent efficiency. The cells are bonded to a BeO substrate, which is subsequently bonded to the Cu heat sink to form a module. Modules of 16 cells each are designed with central plumbing systems to handle the heat load. The array will be tested on the test facility of the other firm.

An alternative concentrator design that uses Fresnel lenses to focus sunlight onto individual cells is also being investigated.

SURVEY OBSERVATIONS

Processing steps appear to be generally well controlled. Because the scale of the operation is limited to laboratory research, evaluation of the processes from an industrial hygiene standpoint is difficult.

The liquid epitaxial growth process appears well controlled. The purge hydrogen is well contained and effective in limiting the possibility of arsenic release. Equipment maintenance and cleaning present greater potential chemical exposure problems. Hydrogen fires and accidental breakage of the glass cylinders present potential problems.

The etching and plating operations are performed in beakers under laboratory hoods. These processing steps are well controlled.

The metallization and antireflective-coating processes are done in vacuum bell jars. The vacuum pumps discharged away from the work area, helping to minimize worker exposure. Bell jar cleaning appears to be the main source of potential metal exposure.

The laboratory areas were crowded with equipment, which indicates the need for a high room ventilation rate. Good ventilation is particularly important because of the toxicity of materials handled, especially arsenic.

PLANT N: GALLIUM ARSENIDE R&D FACILITY-- WALK-THROUGH SURVEY

SUMMARY OF SURVEY FINDINGS

The involvement of Plant N in photovoltaics is focused on research and development work on gallium arsenide (GaAs) concentrator cells. This R&D work spans from polycrystalline GaAs production to module design. The technology level is generally quite sophisticated. Because the materials used are expensive and highly toxic, recovery and containment techniques are elaborate. The broad experience of Plant N in GaAs production and similar technologies is evidenced in the plant's health and safety precautions. This facility was generally well controlled.

PLANT DESCRIPTION

Plant experience with GaAs technology began in the mid-1960's and expanded to photovoltaics about 5 years ago. The major industrial use of GaAs has been in light-emitting diodes (LED's); however, a higher purity is required for photovoltaics.

Areas of research range from Ga and As elemental materials to finished cells. A demonstration, pilot-scale production system is also being developed.

DESCRIPTION OF WORK FORCE

Highly trained scientists and technicians are employed at this plant. Most have had several years experience working with the technology.

MEDICAL, HEALTH AND SAFETY PROGRAM

Plant N employs one physician on a half-time basis and three full-time nurses. A nearby paramedic group is used as needed.

Although Plant N does not have an industrial hygienist, industrial hygiene is among the responsibilities of the plant safety officer. Additionally, one person is responsible for safety in each building. Safety inspections of the entire facility are conducted regularly by a committee of professionals.

All workers in the photovoltaics area are given an initial physical examination. Blood arsenic levels of new employees are checked, and of all employees on an annual basis. Worker medical records are retailed indefinitely.

Air monitoring for arsenic has been conducted in the crystal growth area. Personal monitoring has been done in other work areas.

PROCESS DESCRIPTION

The major cell processing steps are as follows:

Prepare polycrystalline GaAs from Ga and As.

Grow single-crystal GaAs ingots by the Czochralski process.

Slice GaAs into wafers and remove saw damage by polishing.

Grow epitaxial layers sequentially, either by liquid epitaxy or vapor-phase epitaxy.

Perform vacuum metallization of Au/Mg top contact layers.

Perform vacuum metallization of Au/Sn back contact layer.

Perform plasma deposition of Si_3N_4 antireflection layer.

Finished units are designed to be used in concentrator configurations with sunlight concentrations from more than 400:1 to more than 1000:1.

The crosssection of a typical cell is sketched below. Appropriate dopants are added to the substrate and epitaxial layers to make them n+ or p+. The substrate, which consumes the most materials, is 0.36 to 0.41 mm (0.014 to 0.016 in.) thick; the three epitaxial layers total 10 μm (3.9×10^{-4} in.) thick.

Polycrystalline GaAs Production

Gallium in chunk form is loaded into a quartz boat that is placed at one end of a long glass tube. Crushed metallic arsenic is loaded into the other end of the tube, and both ends are sealed in a vacuum. The tube is then inserted into a two-zone tube furnace. The As end is maintained at 610° to 620°C (1130° to 1148°F) and the Ga end is kept at 1250°C (2282°F) [melting point of GaAs is 1238°C (2260°F)]. The As vaporizes and reacts stoichiometrically with molten Ga to form GaAs.

Single-Crystal GaAs Production

Czochralski single-crystal pullers are also used to produce GaAs for photovoltaics. The pullers are located in a room at one end of the research building with a steel door, two concrete block interior walls, and two exterior walls. Crystal growth is monitored with TV cameras located in an adjoining operator control room.

Chunk GaAs is loaded into a quartz crucible with an outer graphite receptor. A liquid boric trioxide (B_2O_3) blanket is maintained over the GaAs. Operating temperature is closely controlled at 1238°C (2260°F) with RF heating coils. Ingots produced are up to 6.4 cm (2-1/2 inches) in diameter.

Wafer Production

A multiblade ingot saw is used to cut the ingot into wafers. A slurry oil is used, which is recycled and lasts a relatively long time. The kerf loss is not recovered. The saw is located under an enclosed exhaust hood.

Wafers are polished in chlorine bleach to remove lap-saw damage.

Liquid Epitaxial Growth

The cell junction layers are added by either liquid or vapor-phase epitaxial growth techniques (the latter is described in the next section). In liquid epitaxial growth (LEG), preweighed metal is added to graphite chambers in an enclosed glass tube. Plant N has designed a semiautomatic technique for sequentially positioning the GaAs wafer in a holder under the chambers and rolling a cylindrical furnace over the tube to melt the metal. A series of melts results in the buildup of a series of different layers. The temperature is kept at 800° to 900°C (1472° to 1652°F) during a melt and is dropped to allow a new layer to form. The layer forms by crystallographic condensation. A hydrogen purge is maintained in the tube. The hydrogen is exhausted through an oil bubbler to a vent duct.

The LEG assembly is equipped with temperature control overshoot. Gallium and arsenic are contained in the graphite, and any arsenic vapor escaping into the H_2 is condensed on the glass walls and a very small amount is collected in the oil bubbler.

Vapor-Phase Epitaxial Growth (VEG)

In this alternative technique for junction formation, the materials needed to form a layer are metered with mass flow controllers into a manifolded stainless steel mixing chamber as organometallic gases. Gases are stored in cylinders. Gases used include: $(CH_3)_3Ga$, $(CH_3)_3Al$, $(C_2H_5)_2Zn$, AsH_3, HCl, H_2S, and hydrogen carrier gas. Wafers of GaAs are loaded onto a coated graphite surface in the reaction chamber. The chamber is cold walled, and growth only occurs at the hot zone. The temperature of the chamber is controlled by RF coils that are wrapped around it. The gas mixture is metered at atmospheric pressure, into the chamber, where the organometallic gases fractionate into metals and hydrocarbons. The metals and dopants deposit out to form an epitaxial layer on the wafers and the gas is exhausted to a sequence of scrubbers.

The reaction chamber develops a thick buildup, which is cleaned with aqua regia.

Cell Fabrication

Metallization is performed with vacuum techniques. The wafer is given a photolithographic resist layer before metallization. After metallization, the metal is thermally alloyed.

The antireflective coating, silicon nitride (Si_3N_4), is added as a plasma in a vacuum chamber.

Plant N has designed a 50-kW GaAs power plant under a U.S. Department of Energy contract with a utility.

ENGINEERING CONTROLS

Polycrystalline GaAs

In the polycrystalline GaAs process, the quartz tube is first loaded with metal, and one end is then fire sealed under N_2 pressure. A vacuum is pulled, and the other end is sealed.

The tube is equipped with a temperature controller that has a overshoot shutoff.

When the tube is in place in the furnace, the hood is closed for the remainder of the cycle.

Single-Crystal GaAs

The major purpose of engineering controls in single-crystal GaAs production is quality control; however, precautions are taken to isolate the pullers from the rest of the building in case of accidental release.

Cleanup includes removing small amounts of arsenic (in the form of As_2O_3) outside the melt. The equipment surfaces are wiped with towels dampened with ammonium hydroxide and hydrogen peroxide.

Liquid Epitaxial Growth

This process is stoichiometrically efficient, and any arsenic released from the quartz tube is removed by passage through an oil bubbler to an exhaust duct.

Vapor-Phase Epitaxial Growth

The exhaust gas passes through the following sequence of chambers:

1. An empty chamber to settle out solids (such as GaAs, As, Ga, Al, Zn).
2. An oil chamber to additionally remove more solid particles.
3. A water solution to collect HCl, H_2S, Ga_2O_3, Al_2O_3, ZnO, and organic metallics.
4. A bromine-water solution to form reactions of AsH_3 to AsBr and finally to As_2O_3, which precipitates out.
5. An NaOH solution to react any bromine carryover into NaBr.

After treatment, the exhaust gas should be almost all hydrogen.

The treatment processes are enclosed in a laboratory hood.

General

Exhaust hoods are provided for all operations.

SPECIAL SAFETY PRECAUTIONS

Operators in the GaAs area are never alone on an operation. This precautionary measure is designed to provide assistance in case of accidents.

All materials purchased go right to the process, especially arsenic, which is transported in glass ampules in the specific quantity needed.

Waste materials are disposed of separately in lined disposal containers. Wastes include arsenic cleaned from outside Czochralski melt, LEG oil-bubbler solution, VEG scrubber solutions, VEG reactor wall cleanup, wafer saw slurry oil, solvents, and acids. Metallic wastes go to an outside firm that handles them from a central disposition point at Plant N. Solvents are drawn under hoods and sent to a disposal company. Acids are neutralized and go to the municipal disposal.

The hydrogen supply is kept outside the building. Plant N uses an automatic H_2 detection system in the area where it is used, with the following capabilities: when the concentration of H_2 in ambient air reaches 0.8 percent, an alarm sounds and the pressure is dropped to 25 percent; at a level of 2 percent the H_2 supply is shutoff and a second alarm sounds. Any sudden change in the pressure drop in the H_2 supply line will shutoff the supply.

OBSERVATIONS AND COMMENTS

Health hazards are minimal because the amount of raw materials processed is relatively small. Gallium arsenide manufacturing and processing are conducted within exhausted enclosures, thereby minimizing the likelihood of emissions to ambient air. (Control of arsenic emissions is particularly important because they could become a serious health hazard.) Personnel exposures are minimized by process controls and careful handling procedures.

The staff at this facility is comprised of highly trained and experienced laboratory and research personnel. They are well aware of potential hazards, the need for care, and proper handling and control procedures. This high capability would not be expected in a larger, production-oriented operation.

The major process steps are conducted in separate areas, isolated from one another. Consequently, materials handling is somewhat more involved than would be necessary or expected in a larger operation.

Crystal growing is conducted in a well-ventilated concrete block enclosure having two outside walls and a steel door connecting to the control room. Television monitors and electronic instruments monitor the process, minimizing the need to enter the crystal-growing room.

Liquid and vapor-phase epitaxy are conducted at about atmospheric pressure. Process steps are conducted within laboratory hoods. Scrubber systems are used to control effluent emissions, which are vented through the laboratory exhaust system. Material flow rates and temperatures are very carefully monitored and controlled.

Protective clothing (gloves, glasses, respirators) are used as necessary during cleaning and handling of the equipment. Cleaning is generally conducted within a laboratory hood.

Crystal cutting operations have local exhaust ventilation. Kerf loss is primarily controlled by capture in a wet slurry.

Laboratory glass and other materials are sometimes cleaned in a special cleaning area by trained and experienced personnel.

Safety procedures are not generally written down, but they are now being drafted. The absence of written procedures is not a serious problem at this facility because of the highly trained personnel. Expansion to industrial production, however, would require the institution of specific policies and procedures on safety and health.

No conditions significantly hazardous to industrial health were found in these limited operations. A followup, in-depth survey is not needed.

The stringency of process controls minimizes potential health hazards.. The high level of personnel further reduces the potential for health and safety hazards.

This and other technologies involving gallium arsenide photovoltaics are not expected to undergo significant changes in terms of work force or industrial hygiene for at least several years. When developments reach the pilot-plant stage, however, industrial health will become a more significant concern.

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