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INDUSTRIAL HYGIENE
WALK-THROUGH SURVEY REPORT
OF
MOTOROLA, INCORPORATED
SEMICONDUCTOR GROUP
PHOENIX, ARIZONA

PHOTOVOLTAICS AREA

Prepared by

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INDUSTRIAL HYGIENE
WALK-THROUGH SURVEY REPORT
OF
Motorola, Incorporated
Semiconductor Group
5005 East McDowell Road
Phoenix, Arizona 85008

PURPOSE: The National Institute for Occupational Safety and Health (NIOSH) is conducting health research studies in various developing energy technologies. An area of rapid anticipated growth is that of photovoltaic solar energy conversion to direct electrical current. This survey is a part of our investigation of this technology. Based on walk-through survey findings, facilities will be chosen for indepth sampling surveys to characterize worker exposures to chemical and physical agents.

DATE OF SURVEY: November 1, 1978

DATE OF REPORT: May 4, 1979

PERSONS CONDUCTING SURVEY: Terry Briggs, Ph.D.
Richard Garrison, Ph.D.
Mark Boeniger

PERSON PREPARING REPORT: Terry Briggs

CONTACTS AT THE PLANT: Mr. Ray White
Development Programs Manager

(602) 244-6366

SUMMARY OF SURVEY FINDINGS

Motorola 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, while production began in the spring of 1977. The photovoltaics area, defined as starting with silicon wafer material is located in one building.

DESCRIPTION OF WORK FORCE

Photovoltaic operators are roughly two-thirds male. Approximately 84% work on the day shift while 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 these are repeated on an annual basis.

PROCESS DESCRIPTION

Motorola's current emphasis in the solar photovoltaics 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 while the photovoltaics scope is from wafer to finished module production.

Polycrystalline Silicon Production

Polycrystalline silicon is produced from trichlorosilane (HSiCl_3) in a separate building and is used primarily in the semiconductor area. HSiCl_3 is stored in nitrogen blanketed tanks outside of the process building. Polycrystalline silicon is formed in chambers by the decomposition of HSiCl_3 saturated in a H_2 stream. The bell jar chambers operated at 1100°C and 7 in. H_2O pressure run for about 230 h per batch cycle. This is a totally closed and highly automated process in which the gas from the chambers, containing contaminants, notably HCl and chlorosilanes, is filtered, compressed to 65 psig, and purified prior

to being recycled. The purification includes a charcoal adsorber to remove HCl and cooling and condensation stages to condense heavy ends. Parallel charcoal chambers are used since the charcoal is regenerated every 6 h.

The chamber room had a very high general ventilation rate with the flow pattern from floor grating up out through ceiling louvres.

Four shut down systems were reportedly installed for emergencies. In case of the chamber glass breaking which normally results in fire, the feed gas and exhaust lines are closed.

Few operators were observed in this area.

Crystal Pulling and Wafer Cutting

These operations were considered to be a 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 Motorola consists of a ribbon growth technique using laser remelt of polycrystalline silicon from silicon vapor deposition. The process sequence consists of a preheat of the silicon ribbon, exposure to two CO₂ laser beams and a post heat. 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 had a 1.2 kW rating. The growth rate was 4 inches per hour.

This process was totally enclosed and shielded.

Wafer Cleaning and Etching

The wafer cleaning and etching operations are primarily for Semiconductor area use, however similar treatment sequences 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 acid solution containing acetic acid, HF, and HNO₃. Cleaning may be performed in a mixture of H₂O₂ - H₂SO₄. 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 centrifuge dried.

Texture Etching

When texture etching is to be employed, Motorola is developing photoresist or wax techniques to mask the wafers. For etching only one side. (Wax masking is discussed later.) In the photoresist process a photoresist material in a xylene base solvent is applied in an exhausted chamber while the wafer is spinning to remove excess liquid. Wafers are then exposed to an ultra violent lamp which develops the photoresist chemicals on one side, allowing dissolution of undeveloped photoresist from the otherside. This process was located in a laminar flow down-draft hood with fail-safe exhaust. Wafers were 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 was used for junction formation on a production level while work on ion implantation is at a near term developmental level.

Seven diffusion furnaces were operated primarily for semiconductor production. After inspecting wafers for defects, they are loaded in cassettes manually into tube furnaces. The diffusion process requires about 90 minutes per cycle in which the furnace temperature is increased from about 900° to 1000°F in various atmosphere. For example, pure H₂ and O₂ are metered in to form steam and also to form a 1 to 1.4 x 10⁴ Å oxide layer on the wafers. Dopants used include BCl₃ and PH₃. The operating cycle is automatically controlled. The silicon nitride surface coating is formed by the thermal decomposition from ammonia and dichlorosilane in the enclosed furnace. The operating cycle is automatically controlled. All cycles have inert gas purges using either N₂ or argon.

Pressure cylinders of O₂, H₂, N₂, BCl₃ and PH₃ are stored at the back of the furnace assemblies with ventilation hoods and equipped with low ventilation flow alarms. The inlet of the tube furnaces were equipped with side-draw ventilation.

The 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. The

implantation occurs in a vacuum chamber using 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 using a pulsed source or a furnace at 900°C maximum. Some metal oxide formation occurs during implantation and is removed using wet chemistry.

Concentrations of all dopant exposures measured have been less than 1 ppm.

Metallization

The metallization pattern is formed by silk screen or photo-resist. By silk screening, the formation of the metallization consisted of first forming silk screen pattern on both sides using a petroleum wax in an isopropyl alcohol solvent. The wax is then baked dry in a vented low temperature oven. The exposed silicon nitride surfaces are etched with an HF-ammonium fluoride mixture. This process is conducted in a laminar flow exhaust hood. Reportedly this process was expensive due both to the high chemical usage and being labor intensive.

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.

Following pattern definition, palladium is plated from two different baths to form a 0.05 micrometer barrier layer.

Following plating of palladium, wafers are then placed into a "sintering tube furnace" in which palladium and silicon are "alloyed" into 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 baths of nickel, palladium and copper salts. These operations are also conducted in laboratory hoods operators wear 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 parrallel and identical process lines are used for panel assembly and testing. Wafers are placed by hand on copper plated panels and then placed 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 the inspection and testing.

The panels are then placed in a degreaser containing isopropanol and methylene chloride. The degreaser is equipped with a vapor trap and has local exhaust ventilation 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 being 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

This process appeared highly automated. The major worker exposure potential appears to be from HCl exposure due to bell jar breakage or maintenance operations if residual chlorosilane remains in opened equipment. This area was not inspected in sufficient detail to adequately be evaluated however.

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 also insure a uniform indraft through the front opening of the hood. Hoods also have a static pressure alarm, with an audible signal in the event of fan failure.

It should be noted that all laboratory hoods have been checked for proper control velocities and airflow patterns by Motorola 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 prior to 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 on. Warning lights and an automatic lock prevent anyone from entering the process room when a laser is on 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 which will shut off all gas cylinders in the event of an exhaust fan failure.

Ion Implantation appeared very well controlled. There is only one operator, who 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 above for diffusion.

After ion implantation, the wafers are placed in high temperature furnace tubes. They 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 via the corridor adjacent to one of the inner walls. Chemicals are placed in ventilated lockers, opening to the hallway and labeled for each type of material to be stored inside. These same lockers also open to the laboratory. In this way, the number of people entering the laboratory is kept to a minimum. Cabinets are two-hour fire-rated and designed specifically for chemical storage safety.

Metallization

These processes are conducted inside laboratory hoods, which were tested and approved by the 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 surveyed, involving the production of solar panels beginning with the silicon wafers, were found to be very well controlled from an industrial hygiene standpoint. 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 to comment on.

A ventilation control and chemical handling philosophy, evident throughout the survey and stated by the Safety Manager, in essence was to provide complete control for every operation and every possible air contaminant. This approach is effective. Against most standards, this facility, as surveyed, would be considered a model to which other industries might aspire.

APPENDIX A

WORK SHEETS COMPLETED
DURING WALK-THROUGH

INDUSTRIAL HYGIENE SURVEY REPORT

Name and Address of Facility Surveyed: Motorola, Incorporated
Semiconductor Group
5005 East McDowell Road
Phoenix, Arizona 85008

Date of Survey: November 1, 1978

Persons Conducting Survey: Terry Briggs, PEDCo Environmental
Richard Garrison, Occusafe
Mark Boeniger, NIOSH

Date of Survey Report: December 27, 1978

Persons Preparing Report: Terry Briggs, Richard Garrison

Purpose of the Survey: Industrial Hygiene Walk Through

Summary of Survey Findings: Photovoltaics activities are primarily focused on R&D work. Commercial scale single crystal silicon production is used primarily for semiconductor area. In general excellent health and safety practices were observed.

Contacts at Facility: (Management and employee Representatives)
(telephone)

(602) 244-5611	Dr. Michael Coleman
(602) 244-6618	Mr. Nick Hild
(602) 244-5479	Dr. Arnie Lesk
(602) 244-5457	Mr. Bob McGinnis
(602) 244-3184	Mr. Dick Pilo
(602) 244-6575	Mr. Sumner Sheff
(602) 244-4053	Mr. Greg Vargo
(602) 244-6618	Mr. Bill Volz
(602) 994-6303	Mr. Ted Werner
(602) 244-6366	Mr. Ray White

II. DESCRIPTION OF FACILITY

1. Brief physical description of plant (including ownership size, number of major buildings, etc): Facility primarily devoted to semiconductor manufacturing. Facilities associated with photovoltaics are in two buildings.

2. Brief Narrative of plant history: (including any product line changes; date built, major changes, etc): Started R&D work in photovoltaics in early 1974 and began production in spring of 1977.

3. Major products or services:

<u>Solar cells</u>	_____
<u>Solar modules</u>	_____
_____	_____
_____	_____

4. Waste products disposal (solid, air, water):

Waste acids are all treated on site

Solvents are collected and reclaimed

Solid wastes are landfilled

III. DESCRIPTION OF WORKFORCE AND PERSONNEL RECORD SYSTEM:

1. A) Number of people on payroll at the present time:

B) Number of people in:	Men		Women
Production Area	_____	2:1	_____
Administrative Area	_____		_____
Other Areas	_____		_____

2. Number of Employees on Shift: 1: _____ Shift 2: _____

Shift 3: _____

84% shift 1; remainder shift 2

3. Narrative Description of Workforce:

Operators, technicians, engineers and administrators

4. Description of personnel Record keeping system:

Medical and accident records are kept by the nurse at each location. Employment record is kept by personnel department.

5. Description and approximate number of workers for each major job category.

3. There is a licensed nurse in this facility at a regular time
 Yes, Full-time X Yes, Part-time No
4. There is at least one employee at this facility on each shift with formal first aid training, other than a doctor or nurse, who has been designated to provide emergency treatment
 Yes X No
5. When new employees are hired they are required to take a medical examination
 Yes, all employees
 Yes, some employees X
6. Periodic physical examinations are provided for employees
 Yes X No How Often Annual
7. Special job related medical tests provided for employees are:
- | | | |
|---------------------|--------------------------|--------------------------------|
| Chest X-Ray | Yes <u> X </u> | No <u> </u> |
| Hearing Tests | Yes <u> X </u> | No <u> </u> |
| Visual Tests | Yes <u> X </u> | No <u> </u> |
| Lung Function Tests | Yes <u> X </u> | No <u> </u> |
| Blood Tests | Yes <u> X </u> | No <u> </u> |
| Urine Tests | Yes <u> X </u> | No <u> </u> |
| Other | Yes <u> X </u> | No <u> </u> |
- Specify
8. A) There is a formal safety program? Yes X No
 B) Safety and Health Supervisor William Volz

C) Number of people involved in Safety and Health program? 3

D) Number of lost-time accidents in this facility last year
Frequency 0 Severity _____

9. Medical abnormalities among workers which can be attributed to an occupational exposure
None

10. Protective equipment which is required:

	Provided by employer	Provided by employee
Clothing	<u>x</u>	_____
Glasses	<u>x</u>	_____
Shoes	<u>x</u>	_____
Respirators	<u>N/A</u>	_____
Type	_____	
Where Used	_____	
Other	_____	

11. A) Facilities for taking showers
Yes _____ No x

B) Facilities for changing clothes
Yes _____ No x

12. Other relevant descriptive information about medical, safety and health program.

V. DESCRIPTION OF PROCESS

Product Silicon solar panels, photovoltaic R&D

Raw materials and possible contaminants:

Metallurgical grade silicon _____

Solvents _____

Acids _____

Production Processes (including major changes; raw materials used in the past; etc).

See Process description

VI. SURVEY OBSERVATIONS:

1. Potential Health Hazards in This Facility

See Report

2. Ventilation and engineering control (Include type, size, kinds of collectors, H.P. of blowers, history of changes, etc.)

All areas are provided with a general air change of 7 changes per hour. Additionally, local exhaust of 100 CFM or more is provided at all chemical use area.

3. Housekeeping:

Excellent

4. Briefly describe any past air sampling data:

5. Comments:

See Report
