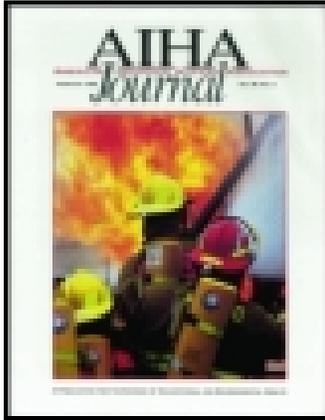


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ASSESSMENT OF ARSENIC EXPOSURES AND CONTROLS IN GALLIUM ARSENIDE PRODUCTION*

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The electronics industry is expanding the use of gallium arsenide in the production of optoelectronic devices and integrated circuits. Workers in the electronics industry using gallium arsenide are exposed to hazardous substances such as arsenic, arsine, and various acids. Arsenic requires stringent controls to minimize exposures (the current OSHA PEL for arsenic is 10 µg/m³ and the NIOSH REL is 2 µg/m³ ceiling). Inorganic arsenic is strongly implicated in respiratory tract and skin cancer. For these reasons, NIOSH researchers conducted a study of control systems for facilities using gallium arsenide. Seven walk-through surveys were performed to identify locations for detailed study which appeared to have effective controls; three facilities were chosen for in-depth evaluation. The controls were evaluated by industrial hygiene sampling, including personal breathing zone and area air sampling for arsenic and arsine; wipe samples for arsenic also were collected. Work practices and the use of personal protective equipment were documented. This paper reports on the controls and the arsenic exposure results from the evaluation of the following gallium arsenide processes: Liquid Encapsulated Czochralski (LEC) and Horizontal Bridgeman (HB) crystal growing, LEC cleaning operations, ingot grinding/wafer sawing, and epitaxy. Results at one plant showed that in all processes except epitaxy, average arsenic exposures were at or above the OSHA action level of 5 µg/m³. While cleaning the LEC crystal pullers, the average potential arsenic exposure of the cleaning operators was 100 times the OSHA PEL. At the other two plants, personal exposures for arsenic were well controlled in LEC, LEC cleaning, grinding/sawing, and epitaxy operations.

The microelectronics industry is expanding the use of gallium arsenide (GaAs) in the production of certain semiconductor devices such as field-effect transistors, microwave integrated circuits, and optoelectronics such as light emitting diodes.⁽¹⁾ However, because the speed of silicon chips has become increasingly faster, GaAs has not replaced silicon in most cases. As a result the rapid growth anticipated for the GaAs manufacturing has not materialized.⁽²⁾

The use of GaAs can create exposure to arsenic, gallium, arsine, and various acids—all of which have potentially severe to moderate health effects. To help understand the extent of these exposures and the means for controlling them, National Institute for Occupational Safety and Health (NIOSH) researchers conducted a study of arsenic exposures and control systems for gallium arsenide operations during 1986-7. Seven walk-through surveys were conducted to identify locations for detailed study which appeared to have effective controls; three facilities were chosen for in-depth evaluation.

This paper summarizes the control measures and arsenic exposures determined for the following gallium arsenide processes: Liquid Encapsulated Czochralski (LEC) and Horizontal Bridgeman (HB) crystal growing, LEC cleaning operations, ingot grinding/wafer sawing, and epitaxy. GaAs crystal synthesis and LEC crystal growth are illustrated in Figure 1.

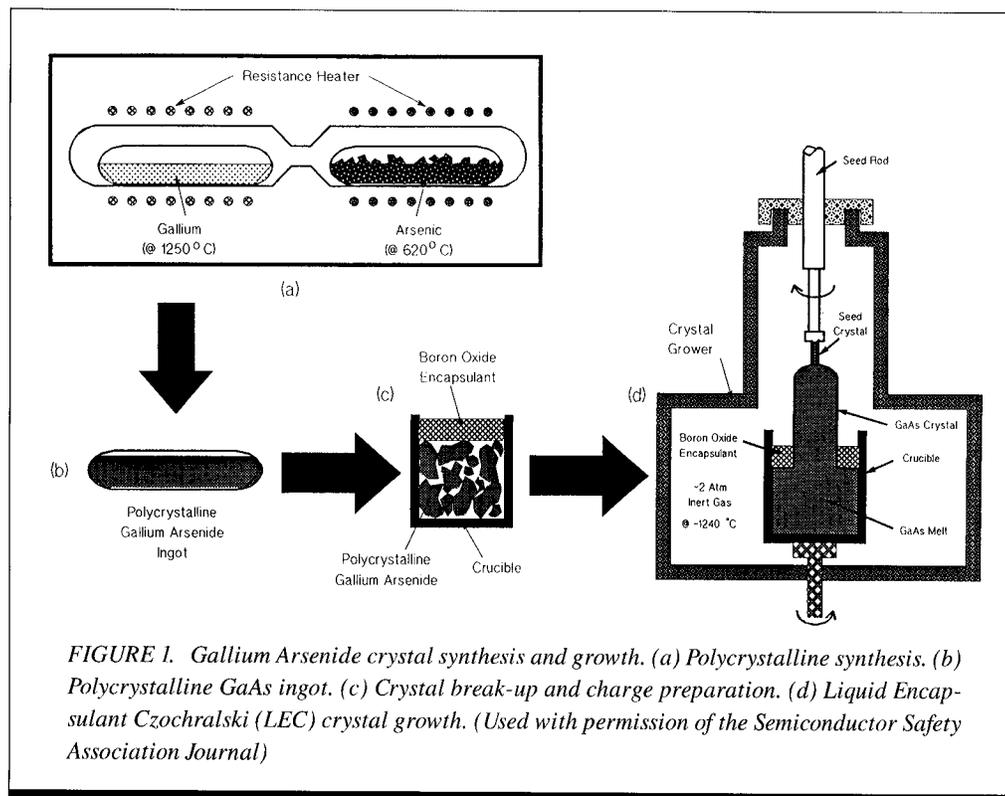
PROCESS DESCRIPTIONS

Plant 1

Plant 1 was a gallium arsenide crystal growing facility which produced, sliced, and polished wafers for use by gallium arsenide optoelectronics, microwave, and integrated circuit manufacturers. The process areas evaluated at Plant 1 during this study are shown in Table I.

At this plant gallium arsenide was synthesized prior to LEC or HB crystal growth. Elemental arsenic and liquid gal-

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lium were loaded into a quartz ampoule and placed in a synthesis furnace. After synthesis, the GaAs charge was cooled, removed, etched, and taken to a cut-off room where surface oxides were cleaned with an abrasive sandblaster and the ends cut off with a saw. In the LEC process, GaAs was loaded into a crucible in one of the crystal pullers and melted at low pressure in the presence of boron oxide. The boron oxide was used to float on top of the melt to help inhibit the release of arsenic vapor. A seed crystal was then lowered into the molten GaAs in its crystal puller and the desired GaAs crystal was grown.

For the HB process, the GaAs charge was broken up in a dry box and loaded into a quartz ampoule. A seed crystal of GaAs was placed into the quartz ampoule, which was evacuated and sealed by a glassblower, and heated in a furnace to form the crystal.

After LEC or HB crystal growth, one side of the ingot was ground flat on a surface grinding machine and the gallium arsenide wafers were sliced from the ingot using automated saws. The wafers were then cleaned before undergoing metal organic chemical vapor deposition (MOCVD) which took place in a Class 1000 clean room. In the MOCVD process, wafers were loaded into a reactor and a mixture of arsine (10 percent concentration), hydrogen (90 percent), trimethyl aluminum, and trimethyl gallium was metered into the reactor chamber with silane and diethyl zinc dopants. A layer of Al-GaAs was then deposited on the GaAs wafer. The general equation⁽³⁾ for this MOCVD process is



Because of the requirement for a high purity product, cleaning of the crystal puller was an integral part of the LEC

process. All internal surfaces of the puller were vacuumed with portable high efficiency particulate air (HEPA) filtered vacuum cleaners and wiped with isopropyl alcohol. (Subsequent to this study, the company switched to a house HEPA-filtered vacuum system for LEC cleaning.) This plant cleaned approximately one crystal puller a day, and changed HEPA filters in the vacuums approximately once a week. The crystal pulling room was designated as an "arsenic regulated area" pursuant to the requirements of the OSHA standard⁽⁴⁾ during cleaning operations.

Plant 2

Plant 2 produced gallium arsenide wafers, field-effect transistors, and monolithic microwave integrated circuits.⁽¹⁾

The processes evaluated at this plant are shown in Table I. GaAs crystals were grown by the LEC technique. Elemental gallium and arsenic were loaded into a boron nitride crucible, which was carried to a crystal puller and placed in a crucible wall support. The gallium and arsenic were melted at high temperature and high pressure in the presence of boron oxide, to produce undoped gallium arsenide ingots. One side of these ingots was then ground flat on a surface grinding machine, and gallium arsenide wafers were sliced from the ingot using automated saws. Next, the wafers were lapped to uniform thickness, polished, and cleaned. In the Vapor Phase Epitaxial (VPE) growth process, which was conducted in a Class 1,000 clean room, thin layers of gallium arsenide were grown on the surface of the wafer. In the VPE process a mix of

Table I. GaAs Processes by Plant

Plant 1	Plant 2	Plant 3
		GaAs Synthesis
LEC crystal growth	LEC crystal growth	LEC crystal growth
Horizontal Bridgeman crystal growth		
LEC cleaning	LEC cleaning	LEC cleaning
Grinding/sawing	Grinding/sawing	Grinding/sawing
Cutoff Operation		
MOCVD Epitaxy	Vapor phase epitaxy	Vapor phase epitaxy

hydrogen chloride, arsine, and phosphine gas with silane dopant gas was metered into a reactor to form the desired layer of gallium arsenide phosphide on the wafer.⁽⁵⁾

The crystal pullers were cleaned following each production run. The graphite insulation was removed from the puller and cleaned with towels and isopropyl alcohol. Each graphite piece was scrubbed with a pad containing a very fine abrasive and vacuumed with a portable HEPA-filtered vacuum cleaner. The graphite liners were then placed in a ventilated contamination control box attached to a wall. All internal surfaces of the puller were then vacuumed (HEPA-filter) and scrubbed with a cleaning pad and isopropyl alcohol. This cleaning procedure required approximately two hours and was performed about two times a week.

Specific housekeeping guidelines were used in the plant. Mops and pails were not allowed to leave the "regulated" crystal pulling area, and the walls and columns in the crystal pulling and epitaxy rooms were vacuumed once a month.

Plant 3

Plant 3 produced optoelectronic devices, specifically light-emitting diodes. Processes evaluated in this study are shown in Table I. Gallium arsenide was synthesized prior to crystal growth. To do this elemental arsenic and liquid gallium were loaded into a long quartz ampoule, which was then placed in a dual temperature synthesis furnace and heated. After synthesis, the polycrystalline GaAs was placed in a low pressure LEC crystal puller, similar to that described for Plant 1. Because of the type of product being manufactured, the pullers used at Plant 3 were smaller than at Plants 1 and 2.

After crystal growth, the GaAs ingot was ground, wafers were sliced from the ingot using automated saws, and the wafers were lapped to uniform thickness, polished, and cleaned. Additional production steps included VPE, and device fabrication. VPE involved loading the wafers into the reactor and metering a mixture of hydrogen chloride, 10 percent arsine (in hydrogen), phosphine (in hydrogen), and diethyl telluride (in hydrogen) into the reactor chamber. A gallium arsenide phosphide (GaAsP) layer was then deposited on the wafer substrate.

The LEC crystal pullers were cleaned following each production run. The cleaning operator opened the puller and removed the gallium arsenide crystal and liners. The parts were cleaned at a ventilated wet chemical station with ammonium hydroxide; quartzware was cleaned in a specialized aqua regia sink. All internal surfaces of the crystal pullers were vacuumed with a HEPA-filtered vacuum cleaner that discharged to the house scrubber and the puller was wiped with wet paper towels. No scraping or scrubbing was involved. Normally, cleaning a single puller took 45 minutes.

METHODOLOGY

Personal breathing zone and area air samples for arsenic were collected on 37-mm diameter cellulose ester filters with an

0.8- μ m pore size, followed by a 600 mg coconut charcoal tube, with a DuPont P-2500 pump operating at a flow rate of 0.5 liters per minute (Lpm). A back-up charcoal tube was employed in areas with heated arsenic sources because of the possible presence of volatilized arsenic. These vapors may pass through conventional sampling filters, hence, monitoring with only a filter could underestimate total arsenic exposures. Use of the charcoal tube limited the flow rate to 0.5 Lpm.

In the cut-off room, a different sampling train, consisting of a 37-mm diameter cellulose ester, 0.8- μ m pore size filter with a DuPont P-4000 pump at a flow rate of 1.7 Lpm was used. The high flow rate was used to obtain sufficient sampling volume because of the short duration of the cut-off room operation.

The cellulose ester filters were pretreated with sodium carbonate and glycerol prior to the conduct of the survey. Larger charcoal tubes (400 mg front/200 mg backup) were used instead of the 100 mg/50 mg charcoal tube stated in NIOSH Method 6001.⁽⁶⁾ The larger tube allowed for longer sampling times at the flow rate of 0.5 Lpm. Charcoal tubes were changed every two to three hours in order to avoid breakthrough. Arsine samples taken in the Epitaxy areas were collected on charcoal tubes (400 mg/200 mg) with a treated pre-filter cassette at a flow rate of 0.1 Lpm using a DuPont P-200 pump.⁽⁶⁾

A personal sampler was attached to the worker's shirt near the breathing zone. Most samples were taken for about an eight-hour shift; however, short-term samples for arsenic were taken for the duration of the LEC cleaning operation.

All filter samples for arsenic were analyzed by graphite furnace atomic absorption spectrophotometry (AA) in accordance with NIOSH Method 7901.⁽⁷⁾ Charcoal tubes were analyzed for arsenic by NIOSH Method 6001⁽⁶⁾ using graphite furnace AA. The limit of detection (LOD) for arsenic was 0.01-0.1 μ g/filter and 0.003-0.07 μ g/tube and the limit of quantitation (LOQ) was 0.04-0.5 μ g/filter and 0.01-0.21 μ g/tube. The LOD and LOQ for arsenic varied with each sample batch; in general, the LOD and LOQ were highest for samples from Plant 1 and lowest for samples from Plant 3.

Because the sampling train used for this study necessitated a 0.5 Lpm flow rate (which is equal to an air volume of only 7.5 liters in 15 minutes), arsenic exposures could not be measured at the NIOSH REL of 2 μ g/m³ (15 minute ceiling) but a 2 μ g/m³ time-weighted-average (TWA) was able to be detected.

Wipe samples also were taken to measure arsenic surface contamination. Wearing disposable polyethylene gloves, an investigator removed a Whatman 42, 7 cm (2.8-inch) diameter filter from the box. The filter was moistened with 0.4 milliliters of triple distilled deionized water using a pipette. Areas of 100 cm² were wiped with the moistened filter. Plexiglas® templates or masking tape were employed to delineate the areas. The filter was folded in half with the exposed side in and folded again to form a 90° angle in the center of the filter. It was placed, angle first, in a clean glass vial and capped for submission to the laboratory. Wipe samples were analyzed by graphite furnace AA in accordance with NIOSH Method

7901.⁽⁷⁾ The LOD for arsenic was 0.08 $\mu\text{g}/\text{filter}$.

During the sampling period, work practices and the use of personal protective equipment were documented, especially during LEC cleaning. Ventilation measurements were taken using either a Kurz or a TSI hot-wire anemometer.

Evaluation Criteria

Inorganic arsenic is strongly implicated in respiratory tract and skin cancer and has been determined to be a carcinogen by NIOSH.⁽⁸⁻¹⁰⁾ In animal studies, GaAs has been shown to dissociate and produce free arsenic. Therefore, NIOSH recommends that gallium arsenide be regarded as a potential occupational carcinogen.⁽⁹⁾ Results from past experiments suggest that GaAs exposure may also result in pulmonary fibrosis.⁽¹¹⁾

Arsenic requires stringent controls to minimize exposures to the current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) of 10 $\mu\text{g}/\text{m}^3$, the OSHA action level of 5 $\mu\text{g}/\text{m}^3$, and the NIOSH recommended exposure limit (REL) of 2 $\mu\text{g}/\text{m}^3$ (15 minute ceiling).^(4,8) The plant also must establish regulated areas in cases where inorganic arsenic exposures exceed the PEL. These regulated areas must be demarcated and segregated from the rest of the workplace, access must be limited to authorized persons, and appropriate respirators must be worn. The OSHA PEL for arsine is 200 $\mu\text{g}/\text{m}^3$, but the NIOSH REL for arsine is the same as the NIOSH REL for arsenic, 2 $\mu\text{g}/\text{m}^3$ (15 minute ceiling).^(4,8)

RESULTS AND DISCUSSION

Crystal Growth

Personal arsenic sample results for the LEC crystal growing area during routine operation are presented in Table II. Arithmetic mean arsenic exposures ranged from 0.6 (Plant 3) to 4.8 $\mu\text{g}/\text{m}^3$ (Plant 1). All arsenic exposures in the LEC area were below the OSHA PEL of 10 $\mu\text{g}/\text{m}^3$ and the arsenic exposures at Plants 2 and 3 were below a TWA concentration of 2 $\mu\text{g}/\text{m}^3$. The highest TWA arsenic exposure in LEC was 8.2 $\mu\text{g}/\text{m}^3$ at Plant 1. In Plants 1 and 3, the LEC puller control consoles were located in the puller rooms, therefore, these workers spent most of their time near the pullers. Although

TABLE II. Personal Exposures to Total Arsenic in LEC

Plant No.	No. of Samples	Average Sample Duration (min)	Arsenic Concentration ^A		
			Arithmetic Mean ($\mu\text{g}/\text{m}^3$)	Geometric Mean ($\mu\text{g}/\text{m}^3$)	Range ($\mu\text{g}/\text{m}^3$)
1	10	254	4.8	4.2	1.4–8.2
2	5	425	0.9	0.6	0.2–2.1
3	4	162	0.6	0.6	0.4–1.2
OSHA PEL		10 $\mu\text{g}/\text{m}^3$			
OSHA action level		5 $\mu\text{g}/\text{m}^3$			
NIOSH REL		2 $\mu\text{g}/\text{m}^3$ (15 minute ceiling)			

^ASum of arsenic collected on filter and charcoal tubes.

TABLE III. Wipe Sample Results for Arsenic

Plant/Location	No. of Samples	Arithmetic Mean ($\mu\text{g}/100\text{ cm}^2$)	Range ($\mu\text{g}/100\text{ cm}^2$)
<i>LEC</i>			
Plant 1	6	260	2–1500
Plant 2 (puller room)	3	970	47–2800
Plant 2 (outside puller room)	1	13	13
Plant 3	3	11	0.4–25
<i>Grinding/Sawing</i>			
Plant 1	3	230	33–580
Plant 2	6	90	6–300
Plant 3	1	11	11
<i>Hall (Background)</i>			
Plant 3	1	4	4

workers at Plant 3 spent most of their time in the room with the pullers and this survey was conducted during one of the heaviest production weeks in LEC (according to plant staff), the LEC operators' arsenic exposures were very low. The production crystal pullers used at Plant 3 were smaller than those at the other two plants, which may explain the lower arsenic levels at Plant 3 during routine LEC operation. The pullers at Plant 2 were located in a separate room from the puller control consoles, and workers spent the majority of their time outside the puller rooms.

Engineering controls in LEC at Plant 1 consisted of general ventilation. At Plant 2 clean HEPA-filtered air was supplied to the control area at a rate of 1.8 air changes per minute and exhausted through the crystal growth room doors. In addition, the separate puller rooms were under negative pressure with respect to the control panel area. At Plant 3 controls consisted of a local exhaust hood (located 13 inches from the center line of each puller) and once through general ventilation. Poor housekeeping also may contribute to increased arsenic exposures (both inhalation and ingestion). Wipe samples for arsenic were collected on various surfaces in the LEC areas at all three plants.

Wipe sample results in micrograms of arsenic per 100 square centimeters ($\mu\text{g}/100\text{ cm}^2$), are presented in Table III.

Arsenic surface Contamination on LEC puller consoles averaged 330 $\mu\text{g}/100\text{ cm}^2$ at Plant 1, 13 $\mu\text{g}/100\text{ cm}^2$ at Plant 2, and 8 $\mu\text{g}/100\text{ cm}^2$ at Plant 3. The much higher arsenic surface contamination at Plant 1 is consistent with the higher arsenic exposures of the LEC operator at Plant 1 versus the Plant 2 and 3 LEC operators (Table II).

Exposures to arsenic in the Horizontal Bridgeman (HB) area (Plant 1), which had only general ventilation, averaged 6.4 $\mu\text{g}/\text{m}^3$ excluding one sample that was 75 $\mu\text{g}/\text{m}^3$. This unusually high exposure may have been the result of an exposure in another process area, since area samples in the HB area averaged only 3.1 $\mu\text{g}/\text{m}^3$. Nevertheless, arsenic exposures in the HB area exceeded a TWA of 2 $\mu\text{g}/\text{m}^3$ and, as in the Plant 1 LEC process, prudent practice indicates the need for regular monitoring and improved engineering controls in these areas.

LEC Cleaning

Personal samples for arsenic collected on the LEC cleaning operators (Table IV) averaged 1070 $\mu\text{g}/\text{m}^3$ at Plant 1. A pressure-demand air-supplied respirator was worn by the cleaning operator and a half-mask, HEPA only, air purifying respirator by the non-cleaning operator who monitored the pullers during cleaning. (The arsenic exposure of the non-cleaning operator averaged 12 $\mu\text{g}/\text{m}^3$ during cleaning.) This difference of two orders of magnitude in potential arsenic exposures between the cleaning and noncleaning operators indicates that the greatest exposure to the cleaning operator came from wiping and vacuuming techniques and other job tasks, rather than from the general room levels during the cleaning process. Area sample concentrations during LEC cleaning averaged 4.0 $\mu\text{g}/\text{m}^3$.

At Plant 2, the average arsenic concentration during LEC cleaning was 430 $\mu\text{g}/\text{m}^3$. The LEC operator wore a full-face (organic vapor/HEPA-filtered dual cartridge) air purifying respirator during cleaning. He also wore disposable coveralls with bootlets, head covering, safety glasses, and disposable latex gloves while cleaning. To prevent contamination of the control area, the operator either put on a clean pair of gloves over the old gloves or removed and disposed of his gloves as he exited the puller room. The pullers were in separate rooms with the control consoles in an adjoining room outside the puller rooms. Area sample arsenic concentrations collected at the control panel during LEC puller cleaning were all less than 1.2 $\mu\text{g}/\text{m}^3$. Isolation of the pullers at Plant 2 protected the LEC workers other than the LEC cleaning operator from arsenic exposures during LEC cleaning. In addition, a down-draft air shower and local exhaust system, designed to move

TABLE IV. Total Arsenic Concentration during LEC Cleaning

Plant No.	Sample Type and Description	No. of Samples	Average Sample Duration (min)	Arsenic Concentration ^A		
				Arithmetic Mean ($\mu\text{g}/\text{m}^3$)	Geometric Mean ($\mu\text{g}/\text{m}^3$)	Range ($\mu\text{g}/\text{m}^3$)
1	Personal ^B	5	71	1070	760	250–2700
	Personal ^C	5	79	12	11	6.9–19
	Area—LEC	10	279	4.0	3.6	1.3–7.5
2	Personal	4	177	430	300	125–1030
	Area—LEC	4	186	58	51	26–107
	Area—Control panel ^D	3	202	<0.8	<0.7	<0.4–<1.2
3	Personal	3	60	0.8	0.6	0.3–1.4
	Area—LEC	6	62	1.0	0.9	<0.6–1.7

^ASum of arsenic collected on filter and charcoal tubes.

^BSupplied-air respirator worn by operator who is cleaning.

^CAir-purifying respirator worn by operator who is not cleaning.

^DThe control panel outside the LEC puller room.

air down over the puller at a rate of 100 feet per minute, was installed above the crystal puller to reduce arsenic levels during cleaning. The worker stood on an exhaust grate directly underneath the air shower system while cleaning the puller. Finally, Plant 2 employed a Plexiglas® contamination glove box with a nitrogen purge as a crucible loading station.

Arsenic exposures at Plant 3 averaged 0.8 $\mu\text{g}/\text{m}^3$ during LEC cleaning. The cleaning operator did not wear a respirator. Based on past results from plant industrial hygiene sampling, respirators were not required during cleaning of the crystal pullers. The HEPA-filtered vacuum cleaner used for LEC cleaning was part of the house exhaust system and vented at a location away from the production room. By contrast, Plants 1 and 2 used portable HEPA-filtered vacuum cleaners that vented into the work area. The use of a central vacuum system may have been one factor contributing to the low levels in Plant 3. This point is supported by the findings from a recent paper¹¹) that the transient generation of arsine may result from a reaction of particulate arsenic and water vapor. The arsine would then pass through the HEPA filter. As a special work practice in the cleaning procedure at Plant 3, the vacuum cleaner hoses and brushes were never placed on the surfaces of the equipment or work tables and were stored in covered plastic cans. This procedure was followed because arsenic contamination on the crystal puller surfaces was documented by wipe sample tests that were conducted by plant personnel. The operator wore latex gloves while cleaning.

Grinding and Sawing

Arithmetic mean arsenic concentrations in grinding and sawing operations, (Table V) for the three plants ranged from 1.3 to 5.3 $\mu\text{g}/\text{m}^3$. All exposures were below the OSHA PEL for arsenic, however, the Plant 1 arsenic exposures were above a TWA of 2 $\mu\text{g}/\text{m}^3$. At Plant 1 the grinding and sawing area consisted of two rooms. In the front room saws were equipped

TABLE V. Personal Exposures to Total Arsenic in Grinding and Sawing

Plant No./Location	No. of Samples	Average Sample Duration (min)	Arsenic Concentration ^A		
			Arithmetic Mean ($\mu\text{g}/\text{m}^3$)	Geometric Mean ($\mu\text{g}/\text{m}^3$)	Range ($\mu\text{g}/\text{m}^3$)
1/Grind/saw	4	312	5.3	4.8	2.1–7.2
1/Cutoff room	3	190	890 ^B	810 ^B	550–1500 ^B
2/Grind/saw	3	155	1.6	1.5	1.0–2.6
3/Grind/saw	4	247	1.3	1.3	1.0–1.7

^ASum of arsenic collected on filter and charcoal tubes.

^BArsenic collected on filter only.

TABLE VI. Personal Exposures to Total Arsine/Arsenic in Epitaxy

Plant No./Process	No. of Samples	Average Sample Duration (min)	Arsenic Concentration ^A		
			Arithmetic Mean ($\mu\text{g}/\text{m}^3$)	Geometric Mean ($\mu\text{g}/\text{m}^3$)	Range ($\mu\text{g}/\text{m}^3$)
1/MOCVD	4	264	<8.9	<8.6	<6.1–<13
2/VPE and annealing	4	299	<2.4	<2.3	<1.7–<3.4
3/VPE	4	370	0.8	0.4	0.1–2.4

^ASum of arsenic collected on prefilter and charcoal tubes.

with local exhaust ventilation (LEV) and an enclosed and ventilated grinder. The back room contained wafer edge bevelers, an enclosed grinder without local exhaust ventilation, a grinder and a saw with LEV, and a saw with an enclosure and LEV. At Plant 2 the surface (flat) grinding machine was provided with an enclosed, wet, recirculation system with a settling tank. This system was vented to wet, packed scrubbers on the roof. The automated saws were partially enclosed and vented to scrubbers on the roof. Two grinders and four inside diameter saws were in the grinding/sawing room at Plant 3. The grinders were equipped with local exhaust hoods. The saws were equipped with a circular enclosure around the saw blade, an exhaust hood positioned below and to one side of the saw blade, and a rubber skirt at the outlet of the saw.

Much higher arsenic levels were measured in the cut-off operation at Plant 1, where the cut-off saw was not enclosed or ventilated and sand blasting was done without an enclosure. Potential arsenic exposure in the cut-off room (Plant 1) ranged from 550–1500 $\mu\text{g}/\text{m}^3$ or up to 750 times a value of 2 $\mu\text{g}/\text{m}^3$. The worker spent about 3 hours each day in the cut-off room and wore a pressure-demand air-supplied respirator; but had he not worn personal protective equipment, his TWA exposure would have been more than 30 times the OSHA PEL for arsenic. Plants 2 and 3 did not have a separate cut-off operation.

The highest arsenic surface contamination in the grinding and sawing operations were 580 $\mu\text{g}/100 \text{ cm}^2$, on the skirting around a saw in Plant 1 and 300 $\mu\text{g}/100 \text{ cm}^2$ on the flat grinder in Plant 2. All other wipe sample results at Plants 1 and 3 showed arsenic surface concentration of less than 100

$\mu\text{g}/100 \text{ cm}^2$. The surface arsenic wipe sample at Plant 3 measured on the top of a work table averaged 11 $\mu\text{g}/100 \text{ cm}^2$. Because there is no standard or recommended allowable level for arsenic surface contamination, surface contamination levels were evaluated by comparing concentrations obtained in rooms/halls outside production areas. A wipe sample taken on a bench in the hall outside the LEC and grinding and sawing production area at Plant 3 showed an arsenic surface contamination of 4 $\mu\text{g}/100 \text{ cm}^2$.

Epitaxy

Personal samples for arsenic (or arsine) collected in the epitaxial area were all below the limit of detection, 8.9 $\mu\text{g}/\text{m}^3$ for Plant 1 and 2.4 $\mu\text{g}/\text{m}^3$ for Plant 2 as shown in Table VI. At Plant 3, the arithmetic mean arsenic exposure in the vapor

phase epitaxy process was 0.8 $\mu\text{g}/\text{m}^3$. Because of the relatively high detection limits for Plants 1 and 2 it is impossible to determine from these data if they were better controlled than Plant 3 or if there were levels of arsenic present that were not detected.

At plant 2, all of the epitaxial growth process (VPE) took place in an enclosed ventilation hood. The air in the epitaxial control room was changed at a rate of 1.3 air changes per minute, by means of a once through air supply system.

The VPE epitaxy operation at Plant 3 was conducted in a bell jar located in an exhausted cabinet. This prevented vapors from escaping into the work area when wafers were unloaded from the bell jar or when the instrument was cleaned. A portable HEPA-filtered vacuum was used during the cleaning process. During the survey of this plant, the exhaust from the portable vacuum was temporarily being directed to an exhausted instrument cabinet, until a dedicated vacuum system exhausted to the outside was installed. The exhaust was discharged into an exhaust cabinet instead of back into the room after plant staff had shown during a previous industrial hygiene study that arsenic vapor, most likely arsine, was being discharged from the portable HEPA-filtered vacuum.

Areas Outside Production

Area arsenic samples collected at Plant 1 in breakrooms and offices, 20 to 60 feet from the process rooms, showed average concentrations of 1.4 $\mu\text{g}/\text{m}^3$ (Table VII). This level indicates cross-contamination between production and nonproduction areas of this plant and may have resulted from general

TABLE VII. Area Arsenic Concentration Outside GaAs Production Rooms

Plant No./ Location	No. of Samples	Average Sample Duration (min)	Arsenic Concentration ^A		
			Arithmetic Mean ($\mu\text{g}/\text{m}^3$)	Geometric Mean ($\mu\text{g}/\text{m}^3$)	Range ($\mu\text{g}/\text{m}^3$)
Plant 1 Hall outside LEC/HB	8	368	1.4	1.4	1.0–1.9
Plant 2 Hall/office across from LEC	4	398	0.4	0.4	<0.4–0.6
Plant 3 Office near LEC & GS	2	373	0.3	0.3	<0.2–0.5
Plant 3 Office in epitaxy	9	402	0.4	0.3	<0.1–0.9

^ASum of arsenic collected on filter and charcoal tubes.

air flow patterns whenever doors to the LEC, grinding/sawing and HB rooms are left open. A separate ventilation system for the breakroom and office areas and less traffic into and out of production areas should help reduce arsenic levels found in nonproduction areas.

At Plant 2, the average concentration for arsenic samples collected in halls and offices outside the LEC and grinding/sawing process rooms was $0.4 \mu\text{g}/\text{m}^3$. Doors to LEC and sawing and grinding were kept closed. Similarly, arsenic levels in an office outside the LEC and grinding/sawing area at Plant 3 averaged $0.3 \mu\text{g}/\text{m}^3$, and the arsenic concentration in an office near the epitaxy area (Plant 3) averaged $0.4 \mu\text{g}/\text{m}^3$. The low arsenic levels at Plant 2 in areas outside production appeared to result from a combination of low arsenic levels in production rooms and keeping the doors to production rooms closed, while at Plant 3 arsenic levels outside production were nearly the same as the low arsenic concentrations in the production area.

Vapor Phase Arsenic

Sampling results showed that in some of the process areas at Plants 1 and 3, a high percentage of arsenic passed through the filter and was collected on the charcoal tube. At Plant 1, the average percentage of arsenic collected on the charcoal tube was 46 percent in grinding and sawing, 31 percent in LEC during regular operation, 16 percent in horizontal Bridgeman, but only 2 percent during LEC cleaning. The percentage of arsenic on charcoal filters in LEC and in grinding and sawing process areas are shown in Table VIII for the three

TABLE VIII. Arsenic Collected on Charcoal Tubes

Plant No.	LEC %	Grinding/Sawing %
1	31	46
2	17	0
3	70	35

GaAs plants. (Any personal and area samples where either the charcoal tube value or the filter value were detectable were included in these results.) At Plant 3, the percentage of arsenic on the charcoal tubes was 70 percent in LEC and 35 percent in grinding and sawing. (Arsenic was detected on 79 of the 145 charcoal tubes at Plant 3.) At Plant 2 arsenic rarely passed through the sampling filter and was found on only 4 of 153 charcoal tubes.

The fact that relatively large percentages of the arsenic measured at Plants 1 and 3 were not collected by the treated filter raises concern about the different forms of arsenic present

during GaAs production and about the sampling method. The sampling method indicates that some of the arsenic collected may be in the form of arsine. The fact that arsenic passed through the filter also raises questions about the use of air-purifying respirators with only particulate (HEPA) filters and the use of HEPA-filtered vacuums that are exhausted into the work area. Currently almost all plants sampling for arsenic are using only filters and therefore would not be aware of the additional arsenic not captured by the filters. As pointed out earlier, transient arsine may be generated by a reaction between arsenic and water vapor and subsequently pass through the filter.⁽¹²⁾

CONCLUSIONS

In general, arsenic exposures during gallium arsenide production for routine operations, including LEC, grinding and sawing, and epitaxy were between the OSHA PEL ($10 \mu\text{g}/\text{m}^3$) and a TWA concentration of $2 \mu\text{g}/\text{m}^3$ for Plant 1. They were mostly less than a TWA concentration of $2 \mu\text{g}/\text{m}^3$ at Plant 2, and were all less than $2 \mu\text{g}/\text{m}^3$ (TWA) at Plant 3. Personal exposures in LEC were well controlled at Plants 2 and 3: Isolating the LEC pullers controlled arsenic exposures at Plant 2; while a smaller production puller equipped with a local exhaust hood may explain the lower arsenic exposures in LEC at Plant 3.

Arsenic exposures in the Horizontal Bridgeman process, an operation found only at Plant 1, were not controlled below a TWA of $2 \mu\text{g}/\text{m}^3$; one personal exposure was above the OSHA PEL. These data indicate the need for improved controls and routine monitoring for arsenic in the HB areas.

Similar arsenic exposures for all three plants were found in grinding and sawing operations, which were enclosed and/or had local exhaust ventilation. The only exception was the cut-off operation at Plant 1, where the cut-off saw was not enclosed or ventilated and the sand blaster was not enclosed in a glove box. The average arsenic level in the cut-off room

was 300 times the average arsenic levels in the grinding and sawing areas of Plants 1 and 3. (The cut-off room operator wore a pressure-demand air-supplied respirator).

There were major differences in arsenic exposures during LEC puller cleaning between Plants 1 and 3 although both plants had similar controls. One difference may be in the LEC process; the product produced at Plant 3 does not require as thorough a cleaning of the puller as do the pullers at other plants. In addition, there are several important differences in work practices. Unlike Plants 1 and 2, no scraping or scrubbing of the internal surfaces of the LEC puller was performed at Plant 3; and HEPA vacuum hoses, when not in use, were stored in covered plastic cans. Plant 2 employed isolation of the pullers and local exhaust ventilation which effectively contained the high levels of arsenic generated during LEC cleaning and prevented increased arsenic exposures at the LEC control consoles.

Arsenic exposures in the epitaxy area were well controlled at Plant 3; but, because of the relatively high detection limits for Plants 1 and 2, it is impossible to determine if they were as well controlled as arsenic at Plant 3. Also, this study did not evaluate many of the MOCVD and VPE cleaning tasks performed by Epitaxy operators.

Relatively high levels of arsenic surface contamination were found in several places: In Plant 1 these were on the base of the LEC puller both before and after cleaning, on an LEC control console, and on the skirting of a saw. In Plant 2 they were on top of an exhaust duct in an LEC puller room. Only minor levels of surface contamination were found at Plant 3. The presence of arsenic surface contamination points to the need for improved housekeeping.

Vapor phase arsenic accounted for a large percentage of total arsenic found for several processes. This arsenic is not collected on filters and would not be seen by most plants that currently sample for arsenic. The fact that this arsenic passed through the filter also raises questions about the use of air-purifying respirators with only particulate filters and of HEPA-filtered vacuums that are exhausted into the work area. A recent study indicates the transient generation of arsine from a reaction of arsenic and water vapor, which then passes through the HEPA-filter.⁽¹²⁾

These conclusions lead to the following specific findings regarding engineering controls and work practices:

1. In general, the Liquid Encapsulated Czochralski (LEC) crystal puller area needs to be physically isolated from other process areas and maintained at negative pressure in relation to surrounding areas to prevent arsenic contamination. Access to the puller area needs to be limited to necessary personnel. However, low arsenic levels measured at Plant 3, indicate that there is no need to physically isolate this plant's smaller size production crystal pullers from the operators' control panel or from other production areas. It is not clear why arsenic levels were lower at Plant 3, therefore, other plants using the LEC process can assume higher arsenic levels unless air sampling results

demonstrate low levels. Additional research may be needed to answer this question.

2. Allowing the LEC puller to cool before opening it for cleaning will minimize arsenic exposures. Use of local exhaust ventilation during cleaning of the crystal pullers will further minimize potential exposure to arsenic. It is best to do the initial cleaning with a HEPA-filtered vacuum cleaner; and any additional wiping or scrubbing is done wet. Graphite liners and other internal parts of the crystal puller can be transferred to an enclosed ventilated hood. Floors and other exposed surfaces are to be wet mopped after completion of puller cleaning.

Wet wiping the contaminated section of the HEPA-filter vacuum hose and storing it in a plastic container between each use cuts down on emissions of arsenic. The cleaning operator can prevent contamination of the control area by removing and disposing of his gloves (or put a clean pair of gloves on over the old gloves) when he exits the puller room.

3. Using a vacuum connected to a house exhaust system which is HEPA-filtered and vented at a location away from the production area may help lower arsenic levels, compared to portable HEPA-filtered vacuum units which may release low levels of arsine into the work area. A recent study shows that adding an activated charcoal canister to an off-the-shelf HEPA-filtered vacuum was effective in removing arsine from the HEPA-filter exhaust.⁽¹³⁾ This type of HEPA vacuum is now commercially available.
4. Where high levels of arsenic are found during LEC cleaning operations, pressure-demand air-supplied respirators with a full facepiece need to be worn.⁽⁹⁾

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