NIOSH ALERT ALERT ALERT ALERT ALERT ALERT

Request for Assistance in

Reducing the Potential Risk of Developing Cancer from Exposure to Gallium Arsenide in the Microelectronics Industry

October 1987

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health

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DHHS (NIOSH) Publication No. 88-100

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REQUEST FOR ASSISTANCE IN REDUCING THE POTENTIAL RISK OF DEVELOPING CANCER FROM EXPOSURE TO GALLIUM ARSENIDE PARTICULATES IN THE MICROELECTRONICS INDUSTRY

WARNING!

WORKERS IN THE MICROELECTRONICS INDUSTRY ARE CAUTIONED THAT INHALATION OR INGESTION OF GALLIUM ARSENIDE PARTICULATES MAY CAUSE CANCER.

SUMMARY

The National Institute for Occupational Safety and Health (NIOSH) is requesting assistance in reducing the potential risk of developing cancer in workers exposed to gallium arsenide particulates in the microelectronics industry. Three recent experimental animal studies have indicated that gallium arsenide dissociates in the body to release gallium and arsenic. The arsenic is inorganic, biologically available, and distributed throughout the body. Inorganic arsenic has been determined by NIOSH to be a carcinogen, whereas gallium, based on available data, is believed to be of low toxicity. Engineering controls, proper work practices, and appropriate personal protective equipment should be used to prevent or greatly reduce the potential for exposure to gallium arsenide. Safety and health officials, editors of appropriate trade journals, and manufacturers of gallium arsenide semiconductor devices are requested to bring these recommendations to the attention of employers, managers, and workers.

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BACKGROUND

Gallium arsenide is used in the microelectronics industry for the manufacture of certain semiconductor devices. The potential exists for exposure to gallium arsenide particulates during the manufacturing process. In 1986, an estimated 94,000 U.S. production workers were employed in the manufacture of all types of semiconductor devices (U.S. Department of Commerce 1986). Gallium arsenide semiconductor devices represent approximately 5.5% of the total semiconductor market (Wood 1986). Data are not available to ascertain the number of workers specifically involved in the manufacture of gallium arsenide semiconductor devices.

No known studies have reported adverse health effects from the exposure of workers to gallium arsenide or gallium particulates. Results from three animal studies demonstrate that gallium arsenide dissociates (separates) into gallium and arsenic in biological tissues. Two of the investigators reported finding unbound inorganic arsenic in the lungs, blood, urine, and feces of gallium-arsenide-exposed animals. The third investigator reported finding both unbound arsenic and arsenic that was chemically bound to organic compounds. Though these data demonstrate that exposure to gallium arsenide represents a source of arsenic exposure, the extent to which arsenic dissociates from gallium arsenide and the mechanism by which this dissociation occurs have not been determined in humans. Inorganic arsenic has been determined to be a carcinogen by the National Institute for Occupational Safety and Health (NIOSH) (NIOSH 1975, 1982). Therefore, since gallium arsenide can dissociate to gallium and arsenic, NIOSH recommends that gallium arsenide be regarded as a potential occupational carcinogen.

RESEARCH REPORTS

Report #1 (Webb et al. 1984)

Webb et al. (1984) reported the partial dissolution of gallium arsenide when tested in phosphate buffers of various ionic strengths (i.e., fluids that are chemically similar to body fluids). In the second phase of this study, a single dose of gallium arsenide partially dissociated when administered either intratracheally or orally to rats, releasing arsenic that was subsequently distributed, depending on the route of administration, to the lungs, blood, urine, and/or feces. Gallium was found only in the lungs and feces, suggesting that some of the dissociated gallium was retained in the lung and that a portion was cleared by the mucociliary clearance mechanism and may have been subsequently swallowed. Qualitative as well as quantitative alterations in urinary porphyrins were reported following the intratracheal administration of gallium arsenide to rats. Webb noted that similar alterations in urinary porphyrins were found by other investigators when inorganic arsenic was administered to rats (Martinez et al. 1983, Woods and Fowler 1978).

Report #2 (Webb et al. 1986)

Webb et al. (1986) administered a single intratracheal dose of gallium arsenide particulates to rats to confirm the dissolution of gallium arsenide and the systemic distribution of arsenic reported by Webb et al. in 1984. Gallium trioxide and arsenic trioxide were also administered intratracheally to rats for comparison with gallium arsenide, since the former compounds are believed to be formed following dissolution of gallium arsenide. Gallium trioxide was observed to have little biologic activity, whereas arsenic trioxide produced some of the same qualitative effects as those noted when gallium arsenide was tested. These results suggest that the most toxic component of gallium arsenide was the arsenic that dissociated from the gallium arsenide after the latter entered the rat's body.

Report #3 (Yamauchi et al. 1986)

Yamauchi et al. (1986) found gallium arsenide to be soluble in phosphate buffers of various ionic strengths as did Webb et al. (1984, 1986). Yamauchi et al. also demonstrated that following oral or intraperitoneal administration of gallium arsenide to hamsters, organic products of arsenic metabolism (dimethylarsinic acid and methylarsonic acid) were found along with inorganic arsenic in the urine and various tissues. These results again demonstrate the dissociation of gallium arsenide and the systemic distribution of inorganic arsenic.

REGULATORY STATUS

No NIOSH or American Conference of Governmental Industrial Hygienists (ACGIH) recommendations or Occupational Safety and Health Administration (OSHA) standards exist specifically for gallium arsenide or gallium. However, the three research reports on animals (Webb et al. 1984, 1986; Yamauchi et al. 1986) demonstrate that there is the potential for arsenic exposure as a result of gallium arsenide exposure in the microelectronics industry. Therefore, the NIOSH recommended exposure limit (REL) for inorganic arsenic (2 micrograms per cubic meter [$\mu g/m^3$] of air as a 15-min ceiling) should be applied (NIOSH 1975, 1982). This short-term limit is intended to achieve the greatest practicable reduction in worker exposure while avoiding spurious sampling results produced by natural background concentrations of inorganic arsenic.

CONCLUSIONS

The NIOSH evaluation of the three published animal studies (Webb et al. 1984, 1986; Yamauchi et al. 1986) concurs with these investigators' conclusions that gallium arsenide dissociates into gallium and arsenic and that the inorganic arsenic is biologically available and distributed throughout the bodies of gallium-arsenide-exposed animals. The toxicological significance of the finding by Webb et al. (1984) that gallium appears to remain in the lungs of gallium-arsenide-exposed animals is not clear and bears further investigation. There is no evidence that gallium arsenide reacts differently in humans. This compound therefore presents the potential for worker exposure to arsenic, a known carcinogen. NIOSH recommends that worker exposure to gallium arsenide be controlled by observing the NIOSH REL for inorganic arsenic (2 $\mu g/m^3$ of air as a 15-min ceiling) (NIOSH 1975, 1982). NIOSH also recommends that the concentration of gallium arsenide in air be estimated by determination of arsenic. This can be done using NIOSH method 7900 for arsenic (NIOSH 1984).

RECOMMENDATIONS

NIOSH makes the following recommendations for minimizing the risk of exposure to gallium arsenide:

- Workers should be made aware of and trained to recognize the hazards of gallium arsenide exposure.
- Engineering controls and work practices should be implemented to reduce gallium arsenide and arsenic exposures in production areas of gallium arsenide semiconductor manufacturing.
- Workers should be provided with and required to use personal protective clothing and equipment.
- Procedures for decontamination, waste removal, transport, and disposal should be established for removing gallium arsenide or arsenic from contaminated materials.

These recommendations are detailed as follows.

1. Awareness and Recognition of Hazards

Policies that address the proper handling of gallium arsenide should be developed and implemented by qualified health and safety personnel. Workers should be trained to recognize the hazards associated with gallium arsenide and to use proper work practices and available engineering controls. Air and wipe samples should be regularly collected from work areas that have the potential for worker exposure to gallium arsenide particulates or that have the potential for surface contamination. These areas include crystal growing, crystal puller cleaning, crystal sawing, and wafer polishing and dicing. The samples should be analyzed for inorganic arsenic. A description of the analytical method may be found in the NIOSH Manual of Analytical Methods, method number 7900 (NIOSH 1984). In some areas of the gallium arsenide process, both arsenic and gallium arsenide particulates may be present.

2. Engineering Controls and Work Practices

The following recommendations for engineering controls and work practices are intended to reduce gallium arsenide and arsenic exposures in production areas of gallium arsenide semiconductor manufacturing.

Crystal Growth -- Quartz ampoules used in horizontal Bridgeman and gradient freeze processes should be enclosed during crystal growth to prevent emissions of gallium arsenide or arsenic in the event of ampoule failure. If such failures occur, contaminated surfaces should be vacuumed with a system that uses a high-efficiency particulate air (HEPA) filter, or it should be wet wiped or both. The use of these HEPA-filtered units requires particular care (personal protective equipment and proper filter disposal) when filters are changed.

Crystal Puller Cleaning -- The crystal puller area should be physically isolated from other process areas and maintained at negative pressure in relation to surrounding areas to prevent gallium arsenide and arsenic contamination. Access to the puller area should be limited to necessary personnel. The puller should be allowed to cool before opening for cleaning to minimize gallium arsenide and arsenic exposures. During the cleaning of crystal pullers for the liquid-encapsulated Czochralski process, local exhaust ventilation should be used to minimize potential exposure to gallium arsenide and arsenic particulates. A HEPA-filtered vacuum cleaner should be used for the initial cleaning. Any additional wiping or scrubbing should be done wet. Floors and other exposed surfaces should be wet mopped after completion of puller cleaning.

Crystal Surface Grinding and Sawing -- The crystal grinding and sawing area should be physically isolated from other process areas and maintained at a negative pressure in relation to surrounding areas to prevent gallium arsenide and arsenic contamination. Access to this area should be limited to necessary personnel. Wet grinding or sawing can reduce particulate emissions from this process, but aerosolization of the gallium-arsenide-contaminated coolant liquid may occur. Thus the coolant catch basin should be enclosed as much as possible. The gallium-arsenide-laden coolant liquid should be properly disposed of. If air and wipe sampling indicate incomplete control of emissions, local exhaust ventilation should be applied to the saw. Floors and exposed surfaces should be wet mopped on a regular basis unless wipe sampling indicates no surface contamination with arsenic.

Wafer Polishing, Backlapping, and Dicing -- Surfaces that may be contaminated should be wet wiped on a regular basis unless wipe sampling indicates that there is no surface contamination with arsenic. If laser dicing is used, local exhaust ventilation should be provided for this operation.

3. Personal Protective Clothing and Equipment

Workers should be provided with and required to use disposable suits, gloves, foot coverings, and other appropriate protective clothing necessary to prevent skin contact with gallium arsenide particulates. This protective clothing should be worn during the cleaning of crystal pullers, crystal growing ampoule failures, and other instances where there may be exposure to gallium arsenide particulates.

Though engineering controls are the preferred method for protecting workers from exposure to gallium arsenide and arsenic, NIOSH recognizes that respirators may be required to provide protection in certain situations such as emergencies and those involving the implementation, maintenance, and repair of engineering controls. If engineering controls cannot adequately reduce exposures below the REL for arsenic, workers should be provided with appropriate respirators.

If respiratory protection is required, the employer should institute a respiratory protection program that meets the OSHA requirements as specified in 29 CFR* 1910.134. In addition to the selection of respirators approved by the Mine Safety and Health Administration (MSHA) and NIOSH, a complete respiratory protection program should include, at a minimum, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning of respirators. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

NIOSH maintains that only the most reliable respirators should be used to protect workers from exposure to workplace carcinogens. Such respirators consist of supplied-air, full-facepiece, positive-

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*Code of Federal Regulations. See CFR in references.

pressure respirators equipped with an emergency self-contained breathing apparatus. The following respirators are recommended:

- A self-contained breathing apparatus with a full facepiece operated in a pressure-demand mode, or

- A supplied-air respirator with a full facepiece operated in a pressure-demand mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand mode.

4. Decontamination and Waste Disposal

Decontamination procedures should be established and implemented where feasible to remove gallium arsenide or arsenic from materials and equipment that have become contaminated. When decontamination is not possible or feasible, the removal, transport, and disposal of materials contaminated with gallium arsenide or arsenic should be in accordance with the regulations of the U.S. Environmental Protection Agency, the U.S. Department of Transportation, and/or State and local authorities.

We urge labor, safety, and trade associations interested in occupational safety and health to bring these recommendations to the attention of workers and employers involved with manufacturing processes that have the potential for gallium arsenide exposure.

Requests for additional information and comments or questions concerning this announcement should be directed to Mr. Richard Lemen, Director, Division of Standards Development and Technology Transfer, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, Ohio 45226, telephone (513) 533-8302. Comments or questions concerning the engineering controls, work practices and the analytical method described in this alert should be directed to Mr. Philip Bierbaum, Acting Director, Division of Physical Sciences and Engineering, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, Ohio 45226, telephone (513) 841-4321.

We greatly appreciate your assistance.

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