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Environmental and Workplace Contamination in the Semiconductor Industry: Implications for Future Health of the Workforce and Community

by Philip Edelman*

The semiconductor industry has been an enormous worldwide growth industry. At the heart of computer and other electronic technological advances, the environment in and around these manufacturing facilities has not been scrutinized to fully detail the health effects to the workers and the community from such exposures. Hazard identification in this industry leads to the conclusion that there are many sources of potential exposure to chemicals including arsenic, solvents, photoactive polymers and other materials. As the size of the semiconductor work force expands, the potential for adverse health effects, ranging from transient irritant symptoms to reproductive effects and cancer, must be determined and control measures instituted. Risk assessments need to be effected for areas where these facilities conduct manufacturing. The predominance of women in the manufacturing areas requires evaluating the exposures to reproductive hazards and outcomes. Arsenic exposures must also be evaluated and minimized, especially for maintenance workers; evaluation for lung and skin cancers is also appropriate.

Background

Over the past few decades the semiconductor industry has grown to encompass many varied processes and chemicals. Once thought of as strictly silicon wafer products, many other substrates, including gallium arsenide, gallium arsenide phosphide, and other combinations now exist. However, formal hazard identification and risk assessment is infrequently reported for facilities manufacturing these devices. Potential health effects have not been analyzed for either the worker or the community.

Silicon Wafer Processes

Processing silicon wafers requires using a myriad of hazardous and toxic chemicals (*1*,*2*). To produce a three-dimensional array of electronic circuits, a photolithographic process is performed that employs various photoactive chemicals in organic solvents including glycol ethers, xylene, and other materials. Once the pattern or mask is exposed on the surface and the protective polymer layer is developed, stripping agents are used to remove the remaining coating. The stripping agents are often phenols or other corrosive and toxic materials.

A silicon dioxide (glass) layer is produced on the wafer in a high-temperature furnace to protect areas of the wafer surface that are not being altered by the deposition of metal ions (doping). Hydrofluoric acid is used to etch this glass surface, exposing a predetermined area to the doping process. Oxidized wafers are dipped in baths of hydrofluoric acid, effectively etching through the glass and exposing the underlying wafer. Exposures to hydrofluoric acid pose a serious hazard and require unique treatment (*3*). Serious burns and systemic fluoride poisoning occurs; death has ensued from seemingly minor burns. High-temperature plasmas are used to etch the wafer surfaces through employing halogenated hydrocarbons.

Semiconductor facilities store and use highly toxic arsine and phosphine and less toxic materials including silanes, halosilanes, and many other exotic gases for various processes. Doping the wafer involves implanting molecular impurities into the crystal lattice structure of the silicon wafer, thus producing electron potentials and therefore circuits. The common dopants include arsenic, phosphorous, boron, and other materials. The arsenic is usually applied in the gaseous arsine form in an ion implanter.

Many health-related issues have emerged as the result of workers being exposed to solvents, glycol ethers,

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radio-frequency radiation, video display terminals, photoactive polymers, metals, and many other materials. Glycol ethers (methoxyethanol and ethoxyethanol) have been the vehicles for the photoactive polymers being applied to the wafer to create an image of the intended circuit. The worker has the potential for exposure to both of these agents during their application and curing. Glycol ethers are teratogenic and have produced reproductive effects in animal studies (*4,5*), even following dermal application (*6*). In animal studies substitution of higher alkoxy groups on the glycol ether appears to prevent teratogenicity. Some chemical suppliers to this industry have already begun substituting these newer agents.

Pastides et al. (*7*) examined reproductive effects in a small number of Massachusetts workers; the results are inconclusive, but they suggest a possible increased, spontaneous abortion rate. The need for further study in the industry was emphasized. Many of the production operators work at computer terminals that control the processes; their exposures to video display terminals have been overlooked, compared with secretarial and other job descriptions. Possible chronic inhalation and dermal exposures to various organic solvents should be evaluated to determine better whether or not this group of workers should be studied for possible long-term hazards (organic brain syndromes) (*8–10*) of solvent exposure. Although the process engineering controls are extreme and impressive, they are designed more for the protection of the product than for the protection of the worker or the environment.

Gallium-Arsenide Processes

A variation from the silicon wafer technology is that of gallium arsenide (GaAs) substrates. Gallium arsenide is a compound semiconductor substrate because it contains more than one element in its base structure. Because gallium arsenide has several times the electron mobility and only a fraction of the electrical capacitance of silicon (*11*), it has many applications for which its speed and power requirements surpass silicon. Gallium arsenide wafers will run six times faster, or alternatively, use one-sixth the energy of a similar silicon device. Gallium arsenide also has greater efficiency for converting light to electron flow and is used in applications in photosensors and photoelectric devices, converting solar power to electrical energy. Gallium arsenide can also be used for light-emitting diodes (LEDs) and for lasers. The low-capacitance gallium arsenide also has potential applications for amplifiers. Compared with the deposition of arsenic in silicon processes, GaAs manufacturing uses more arsine with greater concentrations (up to 100%) during the epitaxial growth of additional GaAs layers on the wafer (*12*).

The wide-scale production of gallium arsenide devices has not yet occurred. Part of the difficulty has been in the production of a sufficiently pure substrate because of inherent difficulties in producing this crystal. Recent technology appears to be overcoming this problem and will continue to allow production and application of these devices in the twentieth century. Gallium-arsenide-based wafers are now used in radar, satellite dishes, microwave transmitters, and solar-powered devices. Other materials used in compound semiconductors include lead, cadmium, tellurium, mercury, antimony, indium, and others.

New advances appear constantly in this highly specialized industry. Although it was once thought that the arsenic in gallium arsenide was immobile and therefore biologically inert, recent studies by Webb (*13,14*) and Yamauchi (*15*) have demonstrated the dissolution and solubility of the arsenic moiety in various chemical milieus. Systemic absorption of arsenic has been demonstrated from gallium arsenide in animal models. This resulted in the *1987 NIOSH Alert, Gallium Arsenide in the Microelectronics Industry* (*16*). The recommendations in this alert included the following statements:

- 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 exposure 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.

It is interesting that this alert did not specifically discuss maintenance operations. Many more companies use premade gallium arsenide wafers than do companies that produce the actual GaAs ingots. Sawing and lapping are important and common processes used to either cut or polish the wafers. Each of these mechanical operations produces a fine and potentially respirable aerosol. Because of the research by Webb and by Yamauchi, concern has developed about this dust production. Generally, the cutting or dicing is performed using wet saws to reduce airborne dust. In addition, wet lapping is used. However, maintenance operations, reactor cleaning, changing the saw coolants and liquids used in the cutting machines, and general housekeeping may expose individuals to respirable, arsenic-contaminated particulates. In addition, spills of the lapping compound, when dried, may produce airborne contaminants. Wet dicing machines that do not properly control the spray have been noted; this results in aerosolized particles that contain gallium arsenide.

Bead blasting of gallium arsenide manufacturing equipment is frequently used for cleaning. During the blasting, which is done in a glove box, the beads themselves become contaminated with arsenic and must be treated as hazardous waste. However, entry into the bead boxes for removing or placing parts for work frequently causes external contamination. This type of entry is a major source of contamination in work areas performing this type of operation.

The production of some specialty devices may require the production of a new layer of gallium arsenide on the preexisting wafer and circuits. This is performed in a large bell jar where operators have placed the wafers. The bell jar is evacuated and subsequently a gaseous environment containing a gallium compound and arsine is allowed to react at high temperature creating the epitaxial layer.

Various parameters of the bell jar and its environment are critical in determining the efficiency of the arsine deposition in the chamber. In general, very small percentages of arsine are actually deposited into the wafer; over 90% becomes waste. Flow rates may be on the order of 400 mL of 100% arsine/min. Therefore, large volumes of arsine or other arsenic compounds must be captured and properly disposed.

Except for the small fraction of arsine actually used for the crystal growth, the arsenic is either deposited on the walls of the reaction chamber and the exhaust system or it is captured in the air-handling systems. The vacuum pump oils are also heavily contaminated. Much of the arsenic may be emitted directly into the environment.

Arsenic and Arsenic Trioxide Production and Waste

After one or more runs, the inside of the reactor (a 3-ft wide, 3-ft high bell jar) must be manually cleaned. This requires that employees scrub the walls of the reaction chamber to remove deposits of arsenic, placing their arms and heads into the dusty enclosure. In many companies this was done by technicians who had not received training either in the hazards of arsenic or in a carcinogen protection program, nor did they have protective equipment. Until recently, many companies did not provide clothes covers, respirators, or other methods of worker protection. Routine industrial vacuums have been used for removing the dust, creating potential airborne contamination because of the lack of sufficient internal seals in nonindustrial vacuums. Subsequent disposal of the vacuum bags into regular trash receptacles has been a common practice.

Arsine cracks (producing arsenic) at approximately 600°C and the temperatures of these reactors is sufficient to effect that reaction. The exhaust flow rates, gas flow rates, vessel temperature, and reactor wall temperature will determine the amount of arsenic deposition on the reactor walls. High-chamber temperatures with cool chamber walls promote the deposition of arsenic in the bell jar. Higher temperature bell jar walls promote the maintenance of a vapor phase and increased exhaust of the arsenic.

Various methods have been used to reduce the environmental impact of effluent arsenic. Material dilution does not reduce the toxic quantity and is not capable of handling many processes or emergency situations. Specific absorptive filters are expensive, cannot handle large sudden quantities, and have a finite capacity requiring frequent monitoring and replacement. Breakthrough is a problem that needs further investigation for adsorptive devices. Wet scrubbing is a method that removes gases, depending on their solubility in a given system. In general, water is used and the water-soluble gases can generally be efficiently removed. Scrubbing is ineffective for pyrophoric gases used in the semiconductor industry, such as silane, and flammable gases like hydrogen. It has variable effectiveness for arsine and other arsenic compounds. Chemicals generally must be added to the scrubbing water to induce the solubility of the arsenic species. Potassium permanganate has been recommended and used in scrubber systems to react with the arsine and oxidize it. The efficiency of this system has not been demonstrated. The contaminated, spent, solutions must eventually be removed and the contaminants must be solidified or otherwise reacted and discarded.

Burn boxes may be used to destroy material such as arsine, but this creates carcinogenic and environmentally hazardous arsenic and/or arsenic trioxide. Novel systems for burning these materials and recapturing arsenic are being investigated and implemented. It is hoped that some of these will permit the recycling of arsenic, therefore minimizing the environmental impact by this system.

The potential for illness related to arsenic is unlikely to be acute or classic. Low-level, chronic exposures are more likely to produce chronic illness and cancers of the respiratory tract and skin. Arsenic has been recognized as an agent capable of causing human cancers by the International Agency for Research on Cancer (IARC) and other agencies. Risk assessments need to be performed in communities where these facilities are in proximity to schools, residences, parks, and other sensitive areas.

New Materials

In addition, because of the extreme toxic nature of arsine gas and the difficulty in handling and transporting this material, manufacturers have sought to produce safer forms of arsenic that may be used for production. Although these arsenic species may have physical and chemical properties that suggest lower toxicity and easier, safer handling, they still will produce arsenic compounds as waste products. The exact toxicity of many of these novel compounds is unknown, and it is unlikely that sufficient quantities of these materials will be produced to allow thorough animal toxicity studies prior to marketing and application. Various other exotic metal coördination complexes that are used in the microelectronics industry likewise have had scant, if any, toxicologic testing prior to their use in research and development.

Waste Streams

The efficiency of effluent gas-stream scrubbing devices is uncertain. Testing one such scrubbing system at a gallium arsenide facility revealed emissions of arsenic at a rate of about 0.05 pounds of arsenic/hr. The effects of flow rate, arsenic concentration, temperature, and other factors on the efficiency of this system have not been documented. The effectiveness of scrubbers is largely unknown in the event of a catastrophic release of contaminant gases into the effluent stream. Yet these facilities are permitted by local air quality districts without a full knowledge of the effects of these variables on system efficiency. All such systems should have emergency power back-up.

As many of these facilities are located in mixed commercial and residential areas, it is possible and probable, over a period of time, that the public health of nearby communities will be affected by these emissions. In several areas of the country, the impact of groundwater contamination by solvents has already had serious effects.

Another source of worker health and environmental impact results from the vacuum pump devices used in the microelectronics industry. The ion implanters, plasma etchers, gallium arsenide reactors, and other devices require extremely low pressures to operate. One or more series of pumps are used to evacuate these chambers. Both the rough pump and diffusion pump may contain various oils or special lubricants. The potential for contamination of these lubricants from the emanating gases flowing through the device has largely been ignored. Although some trade journals (*17*) have discussed the possibility of contamination, it has not become routine in the microelectronics industry to handle vacuum-system lubricants as hazardous wastes. In addition, hazardous materials may also condense or collect in the gas pipeline and plumbing throughout the system.

The assessment of engineering controls in the gallium arsenide industry for worker protection has been undertaken by Jones et al. at NIOSH (*18*). Surveys were performed for the crystal-growing and device-manufacturing operations. Levels of arsenic varied enormously, depending on the type of facility and operation. However, as anticipated, cleaning and maintenance operations appeared to have the highest airborne levels of arsenic, presenting greater risks than those encountered with production processes.

Industrial Hygiene and Biological Monitoring

Environmental air monitoring for potentially toxic materials should be accomplished in the workplace whenever possible. This monitoring is a foundation of industrial hygiene and occupational medicine. However, most of the semiconductor industry has not availed itself of adequate monitoring of its workers. Biological monitoring can also be used to assess internal dose for workers, especially when exposures are difficult to monitor and when dermal absorption of chemicals may occur.

With respect to biological monitoring for arsenic, the traditional use of laboratory analysis of the worker's urine for total arsenic is insensitive. The test is done by hydride generation and atomic absorption of total arsenic. Falsely elevated results occur as a result of in-

Table 1. Potential health effects for semiconductor workers based on hazard identification.

Agent	Workers/jobs	Pathology
Arsenic and arsenic compounds	Maintenance, chemical handlers, ion implanter operators, ion implanter source cleaning	Peripheral neuropathy, abdominal cramps, dermatitis; respiratory tract and skin cancers
Glycol ethers	Photolithography or photo mask operations, maintenance	Acute central nervous system depression, dermatitis, headache, nausea, etc.; reproductive effects including miscarriage and birth defects
Solvents: xylene, mixed hydrocarbons	Photolithography, photo mask operations, maintenance, chemical handlers	Central nervous system depression, headaches, nausea, dermatitis, possible chronic organic brain syndromes
Hydrofluoric acid	Etching stations, maintenance, quartz tube cleaning, exhaust systems workers, chemical handlers	Acute burns that may appear deceptively benign but may be severe and cause life-threatening systemic poisoning; chronic fluorosis not identified in industry
Halogenated hydrocarbons including carbon tetrachloride	Plasma etching, maintenance workers, pump oil handlers	Dermatitis, headache, nausea; elevated hepatic transaminases; possible carcinogenesis (liver?); possibly reproductive hazards and neuropathy
Radio-frequency radiation	Ion implanter devices, plasma etchers and other sources; maintenance personnel	Uncertain effects that may be linked to adverse reproductive outcomes and possibly cataracts
Photoactive polymers	Photolithography or photo mask operations, maintenance	Unknown effects; possible skin or pulmonary sensitization

gestion of nontoxic organoarsenicals found in shellfish and other sources.

The availability of reliable methods for the identification of inorganic arsenic and its metabolites has been a problem. Newer methods of analysis (*19*) will permit accurate assessment of arsenic exposure. Other methodologies will be needed to monitor the exposures of workers, and this industry should support these endeavors.

Summary

The microelectronics industry requires an extremely well-controlled and clean environment for the production of specialized devices. However, this environment is generally designed for the protection of the product rather than the worker or the environment. While the engineering controls may generally provide adequate safety for the process worker, this is not always true. In addition, maintenance operations are frequently unsupervised and poorly planned. Engineering controls protecting the product may incidentally provide worker protection, but they do not afford the same margin of safety for the maintenance workers. Such seemingly innocuous materials as vacuum pump oils may be highly contaminated. Mechanical cleaning of reactors, dicing of wafers, and bead blasting of parts may cause serious contamination within the local environment of the company and for specific workers. An awareness by health care professionals of the potential health effects related to toxic agents in the workplace will assist in the development of properly guided medical and biological surveillance (Table 1).

The efficiency of removal for arsenic-contaminated materials from effluent gas streams is not certain. Improved monitoring technology and removal systems must be developed to minimize emissions. Attention to proper zoning of these manufacturing facilities is mandatory. Biological monitoring affords an additional margin of safety for workers. Worker education, the proper training of production and maintenance workers, emergency contingency measures, and waste stream contaminant analysis are all helpful in protecting workers and the environment. Health care professionals or others interested in a safe and healthful workplace and surrounding community must understand the scope of routine operations and maintenance procedures and continually look for potential exposures.

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