PRELIMINARY SURVEY REPORT:

CONTROL TECHNOLOGY FOR GALLIUM ARSENIDE PROCESSING

AT

Hewlett Packard
San Jose, California

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I. INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) is the primary Federal agency engaged in occupational safety and health research. Located in the Department of Health and Human Services (formerly DHEW), it was established by the Occupational Safety and Health Act of 1970. This legislation mandated NIOSH to conduct a number of research and education programs separate from the standard setting and enforcement functions carried out by the Occupational Safety and Health Administration (OSHA) in the Department of Labor. An important area of NIOSH research deals with methods for controlling occupational exposure to potential chemical and physical hazards. The Engineering Control Technology Branch (ECTB) of the Division of Physical Sciences and Engineering has been given the lead within NIOSH to study the engineering aspects of health hazard prevention and control.

Since 1976, ECTB has conducted a number of assessments of health hazard control technology on the basis of industry, common industrial process, or specific control techniques. Examples of these completed studies include the foundry industry; various chemical manufacturing or processing operations; spray painting; and the recirculation of exhaust air. The objective of each of these studies has been to document and evaluate effective control techniques for potential health hazards in the industry or process of interest, and to create a more general awareness of the need for or availability of an effective system of hazard control measures.

These studies involve a number of steps or phases. Initially, a series of walk-through surveys is conducted to select plants or processes with effective and potentially transferable control concepts or techniques. Next, in-depth surveys are conducted to determine both the control parameters and the effectiveness of these controls. The reports from these in-depth surveys are then used as a basis for preparing technical reports and journal articles on effective hazard control measures. Ultimately, the information from these research activities builds the data base of publicly available information on hazard control techniques for use by health professionals who are responsible for preventing occupational illness and injury.

This particular research effort (the subject of this walk-through survey) was prompted by a growing interest in silicon alternatives for the semiconductor industry. For years, silicon had been the primary semiconductor material for integrated circuits. However, demands for higher speed devices for communication and military purposes led to an anticipated surge in the gallium arsenide technology. Gallium arsenide provides higher electron speeds, lower power consumption, and higher radiation resistivity than silicon.

This study will evaluate the technology available for the control of hazardous substances in gallium arsenide applications, particularly gallium arsenide dusts. The toxicity of gallium arsenide is not well established, but is thought to be similar to that of arsenic. As such, gallium arsenide should be treated as if it were arsenic, which would require stringent controls to maintain exposure to less than the current OSHA standard for arsenic of 10 ug/m^3. Gallium arsenide will require more controls than needed for similar silicon processing. By determining controls needed before major expansion of today's gallium arsenide processing, controls are more likely to be included during construction rather than by costly retrofitting. Specific processes to be evaluated include (but are not limited to) ingot growing, sandblasting, wafer slicing, and the loading, cleaning, and maintenance of epitaxial reactors.

This report contains results of this preliminary study, conclusions, and recommendations relevant to the operations at Hewlett Packard.

II. PLANT AND PROCESS DESCRIPTION

PLANT DESCRIPTION

Hewlett Packard is a gallium arsenide and gallium phosphide production facility, which began operations in early 1984. They produce optoelectronic devices, including light-emitting diodes. In addition, they grow their own gallium arsenide crystals by a low pressure Liquid Encapsulated Czochralski (LEC) technique. Hewlett Packard also does vapor and liquid phase epitaxy.

PROCESS DESCRIPTION

At Hewlett Packard, gallium arsenide (GaAs) is synthesized prior to crystal growth. Elemental arsenic (99.997% pure) and liquid gallium are loaded into a long quartz ampoule, similar to those used in the Horizontal Bridgeman crystal growth technique. The ampoule is then placed in a synthesis furnace and selectively heated for eight hours. After synthesis, the ampoule is opened in a "breakout" station (a glove box) and the polycrystalline gallium arsenide is removed. The crucible is then loaded with the polycrystalline GaAs and placed in the crystal puller. At Hewlett Packard, the polycrystalline GaAs is melted at low pressure in the presence of boron oxide. The boron oxide floats on the melt and serves as a liquid encapsulant to prevent arsenic vapor from escaping. The melt chamber is pressurized with an inert gas atmosphere. A seed crystal is lowered into the crystal puller and the desired gallium arsenide crystal (ingot) is obtained. The entire LEC crystal growth procedure is approximately a 22-hour operation.

After crystal growth, Hewlett Packard checks the crystal orientation of the GaAs ingot with X-ray diffraction. The gallium arsenide wafers are then sliced from the ingot using automated saws. This is a wet process which generates a GaAs slurry that is collected in a separate drain, centrifuged, and partly recirculated. Finally, the wafers are lapped for uniform thickness, polished, and cleaned.

Subsequent steps in the production process include vapor phase epitaxy (VPE) or liquid phase epitaxy (LPE), a nitride deposition, photolithographic processing, and a nitride plasma etching. VPE or LPE is employed depending on the type of product involved. The epitaxial process is performed for the purpose of growing thin layers of other compounds on the GaAs wafers, having the desired electrical properties. For VPE at Hewlett Packard, the wafers are loaded into the reactor and a mixture of hydrogen chloride, ammonia, arsine (in hydrogen), phosphine (in hydrogen), or diethyl telluride gas (in hydrogen) is metered into the reactor chamber. A gallium arsenide phosphide (GaAsP) layer is then deposited on the wafer substrate. For LPE, the same end is accomplished by cooling a heated solution of the above gases while the solution is in contact with the wafer substrate.

After the epitaxially grown layer of GaAsP is completed, a nitride deposition is performed using silane and ammonia. The standard photolithographic procedure follows next where circuit patterns are transferred from a negative (mask) to the surface of the wafer. Additionally, diffusion and aluminum evaporation processing are performed before a second photolithographic procedure. A nitride plasma etch is also performed. Finally, backlapping is done to thin the wafer down in order to allow adequate heat transfer for subsequent operation of the device.

Hewlett Packard also employs a metal-organic chemical vapor deposition (MOCVD) process in which arsine, trimethyl gallium, and trimethyl aluminum are reacted to form a gallium aluminum arsenide layer on the wafer substrate. Hydrogen selenide and diethyl zinc are used as gaseous dopants.

POTENTIAL HAZARDS

Potential chemical hazards in the gallium arsenide industry are found primarily in the numerous solvents, acids, and gases employed in wafer production. At Hewlett Packard, some of the solvents used include fluorocarbon compounds, xylene, and 1,1,1-trichloroethane (TCA). Fluorocarbon compounds can produce mild irritation to the upper respiratory tract. Mild central nervous system depression may also occur in cases of exposure to very high concentrations of fluorocarbons. Liquid xylene may cause irritation to the eyes and mucous membranes. Repeated exposures to xylene through skin contact may cause drying and defatting of the skin which could lead to dermatitis. Liquid and vapor trichloroethane are also irritating to the eyes on contact. In addition, TCA acts as a narcotic and depresses the central nervous system.[1]

Hewlett Packard extensively employs the use of arsine, phosphine, hydrogen, and silane gases for their production processes. Hydrogen selenide (H_2Se) is used only to a limited extent in production. H_2Se is a nose, eyes, and upper respiratory tract irritant. In some cases, pulmonary edema may develop after a latent period of six to eight hours following an exposure. Arsine is an extremely toxic gas that can produce massive hemolysis and renal failure, and exposures as low as 10 ppm have caused coma and death. Early effects from an exposure are characterized by giddiness, headache, shivering, and abdominal pain.[1] Arsine has a slight garlic odor which is only detectable above safe levels.[2] Phosphine is a colorless gas with a characteristic odor of decaying fish and presents a hazard in that it ignites at very low temperatures.[1] If phosphine is inhaled in sufficient concentrations, fatal pulmonary edema may result.[2] Lastly, hydrogen and silane gases present a fire and explosion hazard.

Hydrochloric, hydrofluoric, nitric, sulfuric, and phosphoric acids are also employed at Hewlett Packard in wafer production. These acids may cause burning and scarring of the skin and mucous membranes. Chronic inhalation may cause bronchitis and pulmonary edema.[1]

Chronic exposure to arsenic may cause malaise, fatigue, peripheral neuropathy, and perforation of the nasal septum. Arsenic is also suspected of causing skin and respiratory tract cancer.[2]

Radio frequency exposure may occur during the operation of radio frequency generators or during the plasma etching process. If excessive amounts of radio frequency energy are absorbed by workers, adverse thermal effects may result from the heating of deep body tissue. These thermal effects may include potentially damaging alterations in cells caused by localized increases in tissue temperature.[3]

Finally, trimethyl gallium, trimethyl aluminum, and diethyl zinc lack toxicological assessment to this date.

III. CONTROLS

PRINCIPLES OF CONTROL

Occupational exposures can be controlled by the application of a number of well-known principles, including engineering measures, work practices, personal protection, and monitoring. These principles may be applied at or near the hazard source, to the general workplace environment, or at the point of occupational exposure to individuals. Controls applied at the source of the hazard, including engineering measures (material substitution, process/equipment modification, isolation or automation, local ventilation) and work practices, are generally the preferred and most effective means of control both in terms of occupational and environmental concerns. Controls which may be applied to hazards that have escaped into the workplace environment include dilution ventilation, dust suppression, and housekeeping. Control measures may also be applied near individual workers, including the use of remote control rooms, isolation booths, supplied-air cabs, work practices, and personal protective equipment.

In general, a system comprised of the above control measures is required to provide worker protection under normal operating conditions as well as under conditions of process upset, failure, and/or maintenance. Process and workplace monitoring devices, personal exposure monitoring, and medical monitoring are important mechanisms for providing feedback concerning effectiveness of the controls in use. Ongoing monitoring and maintenance of controls to insure proper use and operating conditions, and the education and commitment of both workers and management to occupational health are also important ingredients of a complete, effective, and durable control system.

These principles of control apply to all situations, but their optimum application varies from case to case. The application of these principles are discussed below.

ENGINEERING CONTROLS

Hewlett Packard uses a combination of general and local ventilation systems to prevent worker exposure to process chemicals. A once-through ventilated system is used in the epitaxy and crystal growing rooms, and a slightly negative pressure is maintained. Ventilated exhaust hoods supplied with high efficiency particulate air (HEPA) filters are used in the production areas for added product and worker protection. The minimum face velocity for the exhaust hoods in these areas is 100 feet per minute (fpm); however, the exhaust hoods for arsenic are generally operated at 125 fpm.

A localized exhaust is also employed behind the crystal puller. This was designed for the situation where a "bad" seed crystal needs to be removed while the puller is still hot.

A gas storage vault is employed for the handling of toxic and pyrophoric gases. This vault contains exhausted gas cabinets with face velocities of approximately 250 feet per minute. Welded stainless steel tubing in ventilated spaces is used for transportation of the gases; and coaxial tubing with a nitrogen purge is used for gases with a pyrophoric rating or toxic gases with concentrations greater than 15%. Waste gases are routed to a segregated ventilation system with a burn box.

Exhaust gases from the epitaxial reactors are vented to a series of scrubber systems. An ethylene glycol-based bubbler and a particulate scrubber trap a high percentage of waste effluents. The remaining waste effluents are trapped by a packed bed water scrubber. The bubbler and the particulate scrubber are employed because otherwise the water scrubber would require periodic maintenance and manual cleaning.

The epitaxial reactors are normally maintained in a hydrogen atmosphere; however, in the event of a power failure, the reactors are automatically switched to a nitrogen atmosphere. Additionally, the valves to the gas cylinders and gas cabinets automatically close.

Hewlett Packard employs seismic bracing of key equipment, such as the epitaxial reactor, in order to prevent the pulling away of gas lines from the reactor.

Drain mechanisms for the ethylene glycol-based bubblers are now located on the back of the epitaxial reactors. However, Hewlett Packard is planning to place the drain mechanisms inside any new epitaxial reactors.

The slicing of the gallium arsenide wafers is a wet process which minimizes emission of GaAs particulate.

WORK PRACTICES

All internal surfaces of the crystal pullers are vacuumed with a HEPA filtered vacuum cleaner. There is no scraping or scrubbing involved. As a special work practice in the cleaning procedure, the vacuum cleaner hoses are placed in plastic cans and never placed on the surfaces of the equipment. This procedure is followed due to contamination on the crystal puller surfaces documented by wipe sample tests.

Operators clean the outside epitaxial reactor plates in a designated stainless steel sink. The gallium trichloride is scraped off and put in a hazardous waste barrel for gallium reclamation. The ethylene glycol-based bubblers are also cleaned in a designated stainless steel sink. All quartzware is cleaned in a specialized aqua regia sink.

MONITORING

Hewlett Packard employs a Telos continuous monitoring system for metal hydride gases and a Rexnord continuous monitoring system for hydrogen in the production areas. In addition, the epitaxial reactors have internal hydrogen monitors.

The facilities department performs ventilation testing on a quarterly frequency. In addition, industrial hygiene sampling and wipe sample testing are conducted regularly.

MEDICAL MONITORING

Preplacement medical examinations are conducted at Hewlett Packard which include blood chemistry testing, urine arsenic testing, audiometric testing, and eye examinations, depending on the employee's job. In addition, medical examinations are provided on an annual basis.

PERSONAL PROTECTIVE EQUIPMENT

In the crystal growing area, operators are required to wear smocks, disposable gloves, and safety glasses. Due to the results from industrial hygiene sampling, disposable respirators are no longer required during cleaning of the crystal pullers. However, supplied air lines are required during the gas cylinder change operation. Self-contained breathing apparatus is available for emergency situations.

OTHER OBSERVATIONS

Hewlett Packard has designated a separate corridor as a "chemical corridor." This is where the chemicals are delivered, loaded into carts, and/or segregated into special cabinets.

Hewlett Packard has developed a fairly extensive training program for their process area employees. This program covers such areas as daily safety practices, including electrical and radiation safety, toxic gas handling, respiratory protection, and emergency response procedures.

IV. CONCLUSIONS AND RECOMMENDATIONS

Hewlett Packard employs relatively small-sized crystal pullers for production compared to other crystal growers we have seen. Worker exposure to GaAs or arsenic dust appeared to be lower during the cleaning operation. However, these small crystal pullers are not typical of the industry and further investigation, in terms of an in-depth survey, may not prove representative of the entire industry.

Hewlett Packard has some useful control measures for limiting the potential exposures to arsenic and toxic gases. This plant may be a possible candidate for an in-depth survey, but other facilities may be more suitable for the purposes of this study.

V. REFERENCES

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