PRELIMINARY SURVEY REPORT:

CONTROL TECHNOLOGY FOR GALLIUM ARSENIDE PROCESSING

AT

M/A-COM
Lowell, Massachusetts

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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 communications and military purposes led to an anticipated surge in 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 requires stringent controls to maintain exposure to less than the current OSHA standard for arsenic of 10 $\mu g/m^3$. 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 M/A-COM.

II. PLANT AND PROCESS DESCRIPTION

PLANT DESCRIPTION

M/A-COM constructed this building specifically for gallium arsenide production and began production in 1984. There are approximately 160 workers. Besides being wafer suppliers, their major products produced include field-effect transistors and monolithic microwave integrated circuits. They grow their own gallium arsenide crystals by the Liquid Encapsulated Czochralski (LEC) technique.

PROCESS DESCRIPTION

For the LEC crystal growth process, the gallium and arsenic are loaded into a pyrolytic boron nitride crucible located within a nitrogen-purged control box. The crucible is then carried to the crystal puller and placed in the crucible wall support. The gallium and arsenic are melted at high temperature and high pressure in the presence of boron oxide. The boron oxide floats on the melt and serves as a liquid encapsulant to prevent the arsenic from escaping. The melt chamber is pressurized with argon. A seed crystal is then lowered into the crystal puller and the desired gallium arsenide crystal is obtained. The LEC technique makes undoped, semi-insulating gallium arsenide ingots.

The cleaning of the crystal puller is an integral part of the LEC process. All internal surfaces of the puller are vacuumed with a HEPA filtered vacuum cleaner and then scrubbed with a Scotch Brite cleaning pad and isopropyl alcohol. This entire cleaning procedure is approximately a two-hour operation, performed up to two times per week.

M/A-COM is also doing some research and experimental work with the Electro Dynamic Gradient (EDG) crystal growth method. This is a hot-walled system which produces highly doped gallium arsenide ingots.

After crystal growth, M/A-COM grinds one side of the ingot flat using a surface grinding machine. The crystal orientation of the ingot is thereby designated. The gallium arsenide wafers are then slowly sliced from the ingot using automated saws. The waste (consisting of butts, cones, and slurries) is removed and sold back to gallium producers for reclamation of the gallium. Finally, the wafers are lapped for uniform thickness, polished, and cleaned.

For production of products other than wafers, additional steps in the production process include epitaxial growth, ion implantation, photolithography, etching, metallization, wafer thinning, wafer scribing, and packaging.

M/A-COM employs the vapor phase epitaxial process for the purpose of growing thin layers of gallium arsenide on top of the wafers. This is done in order to achieve the desired electrical properties. Arsenic trichloride, their arsenic source, is received in sealed glass ampoules, packed in diatomaceous earth. The arsenic trichloride is added to the epitaxial reactor, which is entirely enclosed in an exhausted hood, about once every two months. During operation, hydrogen and silane gas dopant are metered into the epitaxial reactor. A fraction of the total hydrogen contacts the arsenic trichloride liquid which then enters the reactor as a vapor in the hydrogen gas.

The reaction chamber is surrounded by a furnace which heats the arsenic trichloride, a polycrystalline gallium arsenide source, and the gallium arsenide wafers. The arsenic trichloride reacts, in the presence of hydrogen, with the polycrystalline gallium arsenide source. This produces the volatile species of gallium chloride, arsenic (IV), hydrogen chloride, and in smaller quantities gallium trichloride and arsenic (II). The gallium chloride and the arsenic (IV) then react at the gallium arsenide wafer depositing gallium arsenide in a crystalline form. The excess gases are condensed and the residual hydrogen burned off as the gases exit the reaction chamber into an exhausted hood.

The ion implantation process deposits dopants into a gallium arsenide wafer at various depths by accelerating them through an electric field. Silicon tetrafluoride is the gaseous dopant used at M/A-COM. The dopants are ionized by electrical discharge. The beam of ions is focused on the target wafer and strikes the wafer, embedding the ions at various depths. Wafer annealing follows next, where the wafers are heated in a dilute arsenic atmosphere furnace to relieve implantation-induced stress in the crystal lattice.

Photolithographic processes are used to transfer circuit patterns on a negative (mask) to the surface of the wafer. Wet etching is also performed using hydrochloric or nitric acids and small amounts of hydrogen peroxide. For the metallization process, conductive metals such as gold, titanium, or platinum are deposited, in a vacuum, on the wafer. The deposited metal links the circuits together on the wafer in order for it to be functional. The wafers are then thinned. Finally, the wafers are scribed to separate the individual devices on the wafer.

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 M/A-COM, some of the solvents and gases used include methanol, fluorocarbon compounds, silane, and a very small amount of trichloroethylene (TCE) in the wafer manufacturing process. Methanol can cause optic nerve damage and blindness. However, these symptoms occur principally after oral-ingestion of methanol and rarely after inhalation. 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. Silane is a pyrophoric gas and therefore presents a fire and explosion hazard.[1] Trichloroethylene is suspected of causing cancer in humans. However, it is not considered to be a potent carcinogen.[2] Acute exposure to TCE depresses the central nervous system and produces such symptoms as headache, dizziness, fatigue, and nausea.[1] Hydrochloric and nitric acids used in etching processes can cause severe burns to the skin on contact, fumes of these acids can damage the respiratory tract.

Arsine gas is used at M/A-COM in the annealing process. 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.[3]

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.[3]

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

In the LEC process at M/A-COM, cleaning the crystal puller presented the area of greatest risk to the worker and showed the highest arsenic exposures. Therefore, an air shower system was designed and installed above the crystal puller which appears to have significantly reduced arsenic levels. This air shower system moves air down over the puller at a rate of 100 feet per minute. The worker stands on a grate directly underneath the air shower system while cleaning the puller. M/A-COM, not the crystal puller manufacturer, was compelled to design this air shower system in order to reduce the arsenic exposure levels during cleaning. M/A-COM has designated the crystal pulling rooms as a regulated area under CFR 1910.1018.

Each crystal puller at M/A-COM is located in an area that the pressure is held negative with respect to the control area. Clean HEPA filtered air is provided to the control area and is pulled through the crystal growth room doors and exhausted. The air is changed in both areas at a rate of 1.83 air changes per minute. The epitaxial growth operation is conducted in a clean room designed as class 10,000, however, M/A-COM actually operates the clean rooms as class 1,000. All of the epitaxial growth process takes place in an enclosed ventilation hood. The air in the epitaxial control room is changed at a rate of 1.27 air changes per minute, by the means of a once-through air supply system. The primary purpose of the clean room is to prevent contamination of the wafers.

Both the crystal pulling area and the epitaxy laboratory are equipped with an emergency exhaust system which the operator can activate at anytime by pushing a red panic button.

A Plexiglas® contamination control box with a nitrogen purge is employed at M/A-COM as a crucible loading station in the crystal pulling area. The gallium and arsenic are loaded into a crucible located within the glove box. A hazardous waste barrel is provided underneath the glove box for accidental arsenic spills.

The face velocity for the exhaust hoods on the wet chemical stations in the gallium arsenide production area is 150 feet per minute.

While in use, arsine (10.3% concentration) and silane (1,000 ppm) gases are stored in cabinets equipped with a sprinkler system and ventilated at a rate of 150 cubic feet per minute. All welded stainless steel lines are used from enclosure to enclosure for the transportation of these toxic and flammable gases.

A litmus indicator is used on the sealed arsenic trichloride ampoules for the purpose of indicating ampoule leakage or breakage.

The labs have separate drains for solvent and acid/caustic wastes. The acid/caustic wastes are neutralized in an industrial waste treatment system. The solvent wastes are piped to a 1,500 gallon solvent waste storage tank. This makes it much less likely chemicals will be accidentally poured into the sanitary sewers.

The surface grinding machine at M/A-COM is an enclosed, wet, recirculation system with a settling tank. This system is vented to wet packed scrubbers on the roof. The automated saws are partially enclosed and also vented to scrubbers on the roof.

WORK PRACTICES

A special work practice is employed by M/A-COM as part of the receiving procedure for gas cylinders which could be hazardous, such as hydrogen and arsine. A snoop test is performed as the cylinders are taken off the delivery trucks, before acceptance into the plant. If a cylinder is found leaking, it is sent back with the delivery truck. However, if accepted into the plant, the cylinders are placed in ventilated cabinets. One particular group of workers is designated to change the cylinders, whenever needed.

MONITORING

M/A-COM has installed an MDA continuous 24-hour monitoring system for arsine with a sample port in the epitaxy laboratory. A continuous monitoring system for hydrogen is also employed.

Additionally, M/A-COM hired a consultant for technical assistance with engineering controls and aspects of health and safety, and now has a full-time engineer with these responsibilities. In the regulated area, personnel monitoring for arsenic is performed on a quarterly basis.

MEDICAL MONITORING

Preplacement medical examinations are conducted at M/A-COM which include a medical history, spirometry test, blood profile, and a 24-hour urine arsenic test. In addition, annual medical examinations are performed and the 24-hour urine tests are periodically given for people who work in the bulk area.

PERSONAL PROTECTIVE EQUIPMENT

Safety goggles, Tyvek coveralls, shoe covers, and disposable gloves are worn in the crystal growth, epitaxy, and wafer fabrication areas. A full face (organic vapor/toxic particulates, dual cartridge) respirator is required during the cleaning of the crystal puller. Half face respirators are also required during the loading and maintenance of the crystal puller. In addition, supplied air breathing apparatus is required when adding the arsenic trichloride to the epitaxial reactor and when changing arsine cylinders.

OTHER OBSERVATIONS

M/A-COM has developed a very extensive training program for their employees, covering such areas as daily safety practices, chemical and specialized arsenic issues, respirator fitting and training, and right-to-know legislation. They have also prepared several compliance plan documents which outline four general areas: gallium arsenide (GaAs) crystal growth, epitaxial laboratory, GaAs wafer annealing, and wafer and chip fabrication. The training program is provided upon initial employment and at least annually to all employees in these areas.

M/A-COM also follows specific housekeeping guidelines. The mops and pails are not allowed to leave the regulated crystal pulling area. In addition, the walls and columns are vacuumed once a month in the crystal pulling and epitaxy rooms.

IV. CONCLUSIONS AND RECOMMENDATIONS

M/A-COM uses a variety of control measures intended to limit the potential for exposure to arsenic. In particular, they use what seems to be state-of-the-art controls in the crystal growing area which is a major interest in this study. Therefore, M/A-COM will probably be recommended for an in-depth survey to evaluate these control measures.

V. REFERENCES

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3. Doull, J., C.D. Klaassen, M.D. Amdur. Casarett and Doull's Toxicology 2nd Ed. MacMillan Publishing Co., Inc. New York. 1980.