PRELIMINARY SURVEY REPORT:

CONTROL TECHNOLOGY FOR GALLIUM ARSENIDE PROCESSING

AT

Honeywell, Inc.
Richardson, Texas

REPORT WRITTEN BY:
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Division of Physical Sciences and Engineering
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SIC CODE:	3674
SURVEY DATE:	January 13, 1987
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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 $\mu g/m^3$ or the NIOSH Recommendation of 2 $\mu g/m^3$. 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 Honeywell.

II. PLANT AND PROCESS DESCRIPTION

PLANT DESCRIPTION

This plant is a division of Honeywell, Inc., a large manufacturer of electronic devices. This facility is involved in the manufacture of optoelectronic devices, silicon parts, and gallium arsenide integrated circuits. However, the integrated circuit operations are being phased out and equipment transferred to R&D operations in Minnesota because they have not been successful in developing a market for these products.

Honeywell moved into this facility in 1972. The plant is approximately a 140,000 square foot (ft^2) area, with 4,000 ft^2 of the area devoted to gallium arsenide wafer fab production. Honeywell does not grow their own gallium arsenide crystals; they purchase their wafers already sliced and polished. Approximately 70 workers are employed in the wafer fabrication area; one half of the workers are engineers and the other half are production workers.

PROCESS DESCRIPTION

For the production of gallium arsenide integrated circuits, the purchased wafers are cleaned and etched with a sulfuric acid, hydrogen peroxide, and water mix. The wafer is then coated with a silicon nitride layer in a plasma reactor. The nitride is formed in a reaction between silane and ammonia. The ion implantation process follows next, where dopants are deposited into the gallium arsenide wafer at various depths by accelerating them through an electric field. Selenium hexafluoride or silicon tetrafluoride (10% concentrations) are the gaseous dopants used at Honeywell. 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.

Photoresist application is performed by a photo-lithography process in order to define wafer patterns. One of the components in the resist used is 2-ethoxyethyl acetate. Germanium, gold, tin, titanium, and platinum are then used for contact purposes. The deposited metals link the circuits together on the wafer in order for it to be functional. Some of these metals are sputtered using a radio frequency source and some are evaporated. A silicon nitride overcoat is also applied. Dry plasma etching is done with gaseous carbon tetrafluoride, helium, and oxygen. An ion mill is used to remove gold from the wafer. A beam of argon ions is accelerated through the ion mill, striking the surface of the wafer, and knocking off the gold material.

For the production of optoelectronic devices, gallium arsenide or gallium aluminum arsenide layers are epitaxially grown using solid silicon powder and zinc pellets as dopants. A low pressure chemical vapor deposition forms a stable compound (silicon nitride) on the wafer substrate serving as a mask. Silane (1.0% concentration) in hydrogen and ammonia (100% concentration) provide the silicon and nitride sources with nitrogen as the carrier gas.

Negative photoresist application is done by a photo-lithography process. The wafers are developed using developers containing Stoddard solvent, isopropyl alcohol, and n-butyl acetate. The wafers are then immersed in a hydrofluoric acid, ammonium fluoride, and water etchant solution. This removes material that is not protected by photoresist. The remaining photoresist is stripped from the wafer prior to further processing by sulfuric acid-peroxide, or dodecyl benzene sulfonic acid in phenol and 1,2,4-trichlorobenzene solutions.

Oxidation is performed in a furnace using tetraethoxy silane and a zinc solid diffusion is also performed. Hydrochloric acid, sodium hydroxide, ammonium hydroxide, and isopropyl alcohol are used for the post-diffusion furnace cleanup. For metallization, conductive metals such as tungsten (90.0% concentration), titanium (10.0% concentration), and gold are deposited, in a vacuum, on the wafer. Wet etching with potassium iodide then removes the gold. Backlapping is done to remove deposited materials from the backside of the wafer. Acetone and isopropyl alcohol are used for this procedure. The wafers are vapor degreased with 1,1,1-trichloroethane. Finally, the backside of the wafer is sputtered with germanium (12% concentration) and gold.

POTENTIAL HAZARDS

Potential chemical hazards in the gallium arsenide industry are found mostly in the numerous solvents, acids, and gases employed in wafer production. At Honeywell, the solvents and gases mostly used include silane, selenium hexafluoride, tetraethoxy silane, 1,2,4-trichlorobenzene, fluorocarbon compounds, xylene, and 1,1,1-trichloroethane. Silane is a pyrophoric gas and, therefore, presents a fire and explosion hazard. Selenium compounds are strong irritants to the upper respiratory tract and may cause dermatitis to exposed areas. Tetraethoxy silane is a primary irritant to the eyes and nose. Chlorinated benzenes are irritating to the skin and mucous membranes of the upper respiratory tract. Prolonged contact with liquid chlorinated benzenes may cause skin burns. 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 (TCA) are also irritating to the eyes on contact. In addition, TCA acts as a narcotic and depresses the central nervous system.[1]

The glycol ether solvents used at Honeywell include 2-ethoxyethyl acetate. Glycol ethers have the potential to cause adverse reproductive effects in male and female workers and embryotoxic effects, including teratogenesis in the offspring of the exposed, pregnant female.[2]

Hydrochloric, hydrofluoric, sulfuric, nitric, and phosphoric acids are also employed at Honeywell in wafer production. These acids can cause burning and scarring of the skin and mucous membranes. Inhalation can 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.[3]

Radio frequency exposure may occur during the metallization and plasma etching processes. 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.[4]

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

The wafer fabrication operations are conducted in a Class 10 clean room (10 particles or less per cubic foot of air). Most of the processing is done under laminar flow hoods, where the tables are perforated for airflow. The primary purpose of the clean rooms is to prevent contamination of the wafers.

The ventilation in the Class 10 clean room is provided at a rate of 10 air changes per minute with 86% recirculation. A positive pressure is maintained in this room. Air to the clean room is discharged downward through HEPA filters in the ceiling at a laminar flow rate of 100 feet per minute (fpm).

All of the epitaxial growth process takes place in an enclosed ventilation reaction tube. 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.

Ventilation to the total wafer fabrication area includes 18,000 cubic feet per minute (cfm) of fresh, outside make-up air. Face velocities for the exhaust hoods in the gallium arsenide wafer fabrication area are operated at 70 to 100 fpm.

Effluent gases from designated process areas in the wafer fabrication room are exhausted to a segregated scrubber. Acid-using processes are also exhausted to a wet scrubber and the organics-using processes are exhausted only to an activated carbon scrubber. The general room air is not scrubbed.

Exhausted gas cabinets with welded fittings are employed for the handling of pyrophoric and flammable gases.

MONITORING

No continuous hydrogen monitors are employed at Honeywell.

Personnel monitoring for arsenic exposures is performed on a quarterly basis. The corporate industrial hygienist visits this facility once a year. The facilities manager has the general responsibility for maintaining a safe environment.

MEDICAL MONITORING

Preplacement medical examinations are not currently performed. However, Honeywell does conduct urine arsenic testing on a quarterly basis.

PERSONAL PROTECTIVE EQUIPMENT

Safety goggles, Tyvek coveralls, shoe covers, and disposable gloves are worn in the clean room wafer fabrication areas. Nylon gloves are worn for the loading of wafers into the epitaxial reactor.

OTHER OBSERVATIONS

Most of the employee training at Honeywell is "on-the-job" experience. However, Honeywell does show videotapes on chemical handling and safety. Monthly meetings are held where safety aspects and concerns are discussed.

IV. CONCLUSIONS AND RECOMMENDATIONS

This facility was not a crystal grower, which was one of the major interests in this study. The remaining production areas consisted mostly of wafer fabrication which included ion implantation, photolithography, etching, oxidation, metallization, and epitaxy, but these areas did not have any special engineering controls that we would be interested in evaluating at this time.

There was no one at the plant with substantial time to spend for health and safety and only a general awareness of what a good health and safety program includes. We would not propose an in-depth survey at this site.

V. REFERENCES

1. Occupational Diseases - A Guide to Their Recognition, DHEW, PHS, CDC, NIOSH, Cincinnati, Ohio. DHEW (NIOSH), 1977.

2. Glycol Ethers: Current Intelligence Bulletin 39. U.S. Dept. Health and Human Services (NIOSH). May 2, 1983.

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

4. Radio frequency (RF) Sealers and Heaters: Potential Health Hazards and Their Prevention: Current Intelligence Bulletin 33. U.S. Dept. Health, Education, and Welfare (NIOSH). December 4, 1979.