PRELIMINARY SURVEY REPORT:

CONTROL TECHNOLOGY FOR GALLIUM ARSENIDE PROCESSING

AT

Raytheon Company
Northborough, Massachusetts

REPORT WRITTEN BY:
Karen L. Lenihan
James H. Jones

REPORT DATE:
March 1987

REPORT NO.:
ECTB 163-12a

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
Division of Physical Sciences and Engineering
Engineering Control Technology Branch
4676 Columbia Parkway
Cincinnati, Ohio 45226

PLANT SURVEYED:	Raytheon Company 55 Bearfoot Road Northborough, Massachusetts 01532
SIC CODE:	3674
SURVEY DATE:	September 22, 1986
SURVEY CONDUCTED BY:	Karen L. Lenihan James H. Jones, C.I.H. John W. Sheehy, Ph.D.
EMPLOYER REPRESENTATIVES CONTACTED:	Joe Croteau, Facilities Manager Walter Hartford, Division Safety Manager Jim McCarthy, Industrial Hygienist Dave Weir, Manager of Epitaxial Area Dr. Varley L. Wrick, Manager of Gallium Arsenide MMIC
EMPLOYEE REPRESENTATIVES CONTACTED:	Francis O'Malley, Union Steward, IBEW, Local 1505

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 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, and conclusions and recommendations relevant to the operations at the Raytheon Company.

II. PLANT AND PROCESS DESCRIPTION

PLANT DESCRIPTION

This Raytheon facility was founded in 1979 and presently employs approximately 750 workers. The workers are represented by the International Brotherhood of Electrical Workers, Local 1505. The gallium arsenide staff is composed of approximately 55 employees who perform routine production duties and developmental work. In production, Raytheon uses approximately 2,500 grams of arsenic trichloride per year. Raytheon does not grow their own gallium arsenide crystals; they purchase their wafers already sliced.

PROCESS DESCRIPTION

The process operations used to fabricate a gallium arsenide wafer at Raytheon begins in the epitaxy room, a Class 10,000 clean room (10,000 particles or less per cubic foot of air). Two or three inch diameter wafers are unpacked and then cleaned in glacial acetic acid. The wafers are placed in an unheated ultrasonic bath in methanol for approximately a half hour. Afterwards, the wafers are repeatedly rinsed with deionized water and methanol and etched with a "house mix" consisting of 7 parts sulfuric acid, 2 parts hydrogen peroxide, and 1 part water. The wafers are spun dry in a scrubber.

Raytheon has four epitaxial reactors housed in the clean room under Class 100 laminar flow hoods. These reactors are made of quartz, heated with a Lindberg six-zone furnace, and controlled by a microprocessor for sequencing gas flows and temperatures.

For vapor phase epitaxy, the gallium arsenide wafers are loaded into the reactor and thin layers of various substances are grown on the wafers in order to impart the desired electrical properties. Arsenic trichloride, the arsenic source, is contained within 100 gram ampoules. The sealed ampoules are carried to the reactor glove box, where they are cut, scribed, and broken for use. The contents of the ampoule are poured down a funnel to a hydrogen bubbler. The emptied ampoules are then stored within the glove box. In the bubbler, hydrogen gas entrains the arsenic trichloride, and passes to the reactor tube. Hydrogen and silane gas dopant are also brought into the epitaxial reactor and combined with a polycrystalline gallium arsenide source to form gallium chloride. The gallium chloride and the arsenic trichloride are heated in the furnace releasing gallium and arsenic atoms. These atoms are deposited on the gallium arsenide wafers and crystallized. The excess hydrogen and chlorine passes out of the reactor as hydrogen chloride gas.

Other steps in the production process consist of photolithography, etching, and metallization. Photolithographic processes are used to transfer circuit patterns on a negative (mask) to the surface of the wafer. The solvents used in the photolithography process at Raytheon include methanol, isopropanol, acetone, xylene, trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), n-butyl acetate, glycol ether solvents, and limited use of chlorobenzene. Dry plasma etching is used at Raytheon in addition to wet etching. The plasma etching system uses fluorocarbon compounds or oxygen to produce a chemical species that will etch the surface of the wafer. In the metallization process, conductive metals such as nickel, gold, 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. In addition, Raytheon has a new low radio frequency sputterer in development for metal deposition.

Next, the gallium arsenide wafers are scribed into four pieces and mounted on a lapping block with oil. The lapping process is performed to thin the wafers down to a thickness of approximately 2-1/2 mils. The process is completed within one and a half hours. After lapping, another mil is etched off the wafer with a mixture consisting of 3 parts sulfuric acid, 1 part hydrogen peroxide, and 1 part distilled water. However, the wet lapping process is a time-consuming method, so a new continuous-feed wafer grinder is currently being installed at Raytheon. It will thin the wafer down from a thickness of approximately 22 mils to 4.1 mils after the front circuitry is completed on the wafer. Wet etching would then remove an additional 0.1 mil off the wafer. The wafer grinder is predominantly an enclosed wet system that has a settling tank which would require periodic cleaning. Finally, an automatic dicing saw is used to dice the wafers with deionized water added as a lubricant.

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 Raytheon, the gases used in the epitaxy room include hydrogen, helium, and silane. Hydrogen and silane present a fire and explosion hazard. In addition, the solvents used in the photolithography process present the following hazards: Methanol can cause optic nerve damage and blindness. However, these symptoms occur principally after oral-ingestion of methanol and rarely after inhalation. 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. In addition, acute exposure to xylene vapor may cause central nervous system depression and minor effects on the liver and kidneys. Acute exposure to trichloroethylene also depresses the central nervous system and produces such symptoms as headache, dizziness, fatigue, and nausea.[1] TCE is suspected of causing cancer in humans.[2] However, it is not considered to be a potent carcinogen. Liquid and vapor TCA are irritating to the eyes on contact. In addition, TCA acts as a narcotic and depresses the central nervous system. Acetates are irritants to the mucous membranes in short-term exposures. Prolonged overexposures can produce irritation of the skin.[1] The glycol ether solvents at Raytheon include 2-methoxyethanol (2ME) and 2-ethoxyethanol (2EE). 2ME and 2EE 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.[3] Finally, chlorobenzene is a skin, eyes, and nose-irritant and is known to cause liver and central nervous system damage.[1]

Hydrochloric, hydrofluoric, sulfuric, nitric, and phosphoric acids are also employed at Raytheon 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 including arsenic trichloride may cause malaise, fatigue, peripheral neuropathy, and perforation of the nasal septum. Arsenic is also suspected of causing skin and respiratory tract cancer.[4]

Radio frequency exposure may occur during the metallization 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.[5]

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

At Raytheon, the epitaxial and photolithographic operations are conducted in Class 10,000 clean rooms with most of the processing done under Class 100 laminar flow hoods. The primary purpose of the clean rooms is to prevent contamination of the wafers.

The ventilation in the epitaxy room is provided at a rate of 105 air changes per hour with 59 percent recirculation and a slightly positive pressure is maintained in the room. Of the approximately 18,000 cubic feet per minute (cfm) of air exhausted, 7,000 cfm is exhausted through the exhaust hoods to a scrubber. Recirculated air is returned back through the wall registers and ductwork to 99.99% high efficiency particulate air (HEPA) filters in the ceiling.

Face velocities for the exhaust hoods in the gallium arsenide production area are high. The hoods are operated at 150 feet per minute.

A local exhaust scavenging hood was designed and installed over an end cap of the epitaxial reactor. This was done in order to protect the worker while unloading the wafers from the reactor.

At Raytheon, the primary safety hazard to guard against in the epitaxy area was the droppage of the arsenic trichloride ampoules while being transported to the reactor. In an emergency situation, an automatic cut-off switch was employed to shut down the general ventilation, while leaving the exhaust operating.

Silane was stored in ventilated cabinets in a room adjacent to the epitaxy room. A hydrogen and 0.1% silane mixture was piped to the epitaxy room, and this 1/4-inch tubing was exposed on the wall and on a mixing table, leaving it open to possible damage. Compression fittings were used on some connections. This type of fitting is subject to leaks and an undetected leak in the hydrogen and/or silane lines could lead to a fire or explosion. This is especially the case since there are no continuous air monitors for hydrogen used here.

The new wafer grinder operation was located in a room that had general building ventilation, provided at a rate of approximately 750 cfm.

Interlocks will be placed on the new radio frequency sputterer which was under development for metal deposition. The interlocks will prevent operation of the generator if the cabinets are mistakenly left open.

WORK PRACTICES

A special work practice is employed in preparing the aqua regia solution used for cleaning the gallium arsenide wafers. The aqua regia solution is mixed in the evening when the majority of employees are gone.

Another work practice is employed as a safety precaution in the event of ampoule droppage. The arsenic trichloride ampoules are enclosed within plastic containers and these plastic containers are not removed until the ampoules are placed in the reactor glove box.

MONITORING

Air sampling is not routinely performed by Raytheon, but it has been conducted in specific process areas by an insurance carrier. Some exposure data obtained from a previous sampling survey conducted by the insurance carrier is presented below.

Personal sampling for the operators in the epitaxy room showed arsenic concentrations below detectable limits (less than 0.002 mg/m^3). Source samples taken inside the wafer unloading/reloading hood also indicated arsenic levels below detectable limits (less than .001 mg/m^3). Arsine was also sampled for in the general room air, at breathing zone level, during removal of a gallium arsenide wafer from the reactor and the reloading of a wafer to the reactor. These grab samples were below detectable limits for arsine.

MEDICAL MONITORING

A full-time occupational nurse is employed onsite. In addition, pre-employment examinations are given routinely.

PERSONAL PROTECTIVE EQUIPMENT

Polyvinyl chloride (PVC) gloves are used during the chemical and acid handling necessary for the cleaning of the gallium arsenide wafers. Safety glasses and PVC gloves are also required for workers in the epitaxy area, in particular during the transport of ampoules to the reactor.

IV. CONCLUSIONS AND RECOMMENDATIONS

A few changes in Raytheon's monitoring program could be made in order to ensure that occupational exposures to solvents, gases, and gallium arsenide dusts are appropriately controlled. Although Raytheon has established baseline exposure data with an insurance carrier, a program for air sampling should be established to encompass any process changes or additions. Wipe samples for arsenic should also be taken in order to determine levels of surface contamination.

The network of piping exposed on the wall of the epitaxy room presents a potential for a major release of explosive or flammable gases. The piping network should be better protected and any variation from welded lines (for example, valves) should be enclosed in ventilated spaces.

Raytheon will probably not be recommended for an in-depth survey. However, a final decision will not be made until all of the preliminary surveys are completed.

V. REFERENCES

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

2. NIOSH Recommendations for Occupational Safety and Health Standards, Morbidity and Mortality Weekly Report, U.S. DHHS, CDC, NIOSH Vol. 35, No. 15, Atlanta, Georgia, September 26, 1986.

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

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

5. Radiofrequency (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.