Primer on Compound Semiconductor Environmental, Health and Safety Challenges

Brett Jay Davis, Motorola, Austin, TX, USA

ABSTRACT

The compound semiconductor industry manufactures an array of semiconductor products on substrates other than silicon oxide. The chemicals used and the wastes generated by this industry are often different in quantity and type from those in the silicon oxide semiconductor industry. The hazards of these substrates, chemicals and wastes result in the applicability of a host of environmental, health and safety (EHS) programmes, driven domestically and internationally by governmental agencies, professional and standards organisations, and customers. This article will discuss the hazards of the substrates, chemicals and wastes and identify many existing and pending programmes applicable to them. New waste treatment technologies are discussed and support organisations for EHS professionals in the compound semiconductor industry are listed.

SUBSTRATES PHYSICAL AND HEALTH HAZARDS

Gallium arsenide and indium phosphide are among the more common substrate materials utilised in the compound semiconductor industry. These materials themselves have significant health and physical hazards for which many EHS programs apply.

The toxicological information for gallium arsenide (GaAs) is derived from the hazards of arsenic, as gallium has low toxicity. The most common exposure route for gallium arsenide is inhalation of particulates. Gallium arsenide has a very low threshold limit value (TLV) of 0.01 mg/m³ or 10 µg/m³, as arsenic, and is considered a human carcinogen.

The toxicological information for indium phosphide (InP) is derived from indium. The most common route of exposure is inhalation of particulates. Indium phosphide has a very low threshold limit value of 0.01 mg/m³, as indium. Target organs are the liver, heart, kidney, blood and lungs. This material, which is itself flammable, can react with water vapour and acids to form phosphine, which is a toxic and flammable gas.

PROCESS CHEMICALS PHYSICAL AND HEALTH HAZARDS

Table 1 lists the health and physical hazards of many process chemicals used in the compound semiconductor industry. The toxic, flammable and pyrophoric characteristics of many of these chemicals result in the applicability of many EHS programs for their storage, use and waste disposal.

ENVIRONMENTAL REGULATORY PROGRAMS CHALLENGES

In the United States, many environmental acts have been promulgated, resulting in regulations enforced by the Environmental Protection Agency (EPA) or state environmental agencies.

The Clean Water Act (CWA) establishes requirements for the quality of waste water and storm water discharges. Most industrial facilities discharge to a publicly owned treatment works (POTW), which establishes permit limitations for discharges from those facilities. Generally, semiconductor facilities need only raise the pH of industrial wastewater discharges to comply with POTW requirements. However, compound semiconductor operations manufacturing gallium arsenide must also meet arsenic discharge standards, typically on the order of 100 µg/l. Table 2 lists a variety of treatment technologies that have been successfully used to meet this standard.

The Safe Drinking Water Act gives the EPA the authority to regulate the quality of drinking water. The EPA is presently considering lowering the maximum contaminant limit (MCL) for arsenic to 50 µg/l. This drinking water standard will likely become the industrial waste water standard, which would result in the need to use the more robust, efficient and expensive treatment technologies, such as membrane separation.

The CWA also mandates control of storm water discharges from many industrial facilities. Permits are required that include requirements for best management practices (BMP) and storm water pollution prevention plans (SWPPP). All semiconductor facilities must comply with the requirements applicable to the electronics industry, which includes quarterly storm water sampling and specific limits for listed metals.

The Clean Air Act (CAA) establishes limits for discharges of chemicals, including combustion by-products, into the air. New source review (NSR) permits are required prior to construction of industrial facilities with air emissions. More restrictive permits, known as federal operating (Title V) permits, are required of facilities with emissions above the major source thresholds for hazardous air pollutants and criteria pollutants. Arsenic and phosphorus are both hazardous air pollutants and semiconductor facilities can emit large quantities of nitrogen oxides (NOx) and carbon monoxide (CO). Presently, the
Semiconductor Industry Association (SIA) and EPA are negotiating on maximum achievable control technology (MACT) for semiconductor industry major sources. Table 3 lists abatement technologies that have been used to treat arsine and phosphine emissions.

The CAA also establishes the risk management program (RMP) that is designed to protect the public and environment from catastrophic releases of toxic chemicals. This program requires a hazard assessment, prevention program, emergency response plan, risk management plan and extensive record keeping. Ammonia, arsine, chlorine, diborane, hydrogen, hydrogen chloride, hydrogen fluoride, methane, nitric acid, phosphine and silanes are listed in the RMP rule. The applicability thresholds for arsine and phosphine are only 100 pounds. In addition, the general duty clause (GDC) applies to all hazardous materials, not just those listed in the RMP rule.

The Resource Conservation and Recovery Act (RCRA) establishes the “cradle to grave” waste disposal procedures that incorporate a waste manifest system. Also applicable to semiconductor operation are Subparts BB and CC, which require programs for preventing solvent emissions to air from waste solvent collection and storage systems.

The Toxic Substances Control Act (TSCA) establishes requirements for “new chemical” production and import/export controls. Presently, SIA and EPA are in negotiations to allow continued use of perfluorooctyl sulfonates (PFOS), which are important components of photo resists used by the compound semiconductor industry. TSCA also requires that new health effects from chemical exposures in the work place be reported.

The Emergency Planning and Community Right to Know Act (EPCRA) requires reporting of chemical storage and releases. Chemical storage of listed chemicals is required using “Tier II” forms submitted to the Local Emergency Planning Committee (LEPC) and the local fire department. Annual discharges must be reported for a short list of chemicals using the “Toxic Release Inventory” (TRI) forms. Also, Federal and local emergency notification procedures are established for accidental releases into the environment. TRI reporting for persistent bioaccumulative toxins (PBT), ozone (which is not well destroyed in exhaust handling and treatment systems), nitrates discharged into waste water, and lead from final manufacturing activities should not be overlooked by semiconductor manufacturers.

### Table 1. Physical And Health Hazards Of Compound Semiconductor Process Chemicals

<table>
<thead>
<tr>
<th>Compound</th>
<th>MP (°F)</th>
<th>BP (°F)</th>
<th>Flame range</th>
<th>TLV (ppm)</th>
<th>IDLH (ppm)</th>
<th>Significant Hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂H₆</td>
<td>-165</td>
<td>-92</td>
<td>Pyrophoric</td>
<td>0.1</td>
<td>15</td>
<td>Highly toxic, pyrophoric</td>
</tr>
<tr>
<td>CH₄</td>
<td>-182</td>
<td>-164</td>
<td>5 – 14</td>
<td></td>
<td></td>
<td>Asphyxiant, flammable</td>
</tr>
<tr>
<td>NH₃</td>
<td>-78</td>
<td>-33</td>
<td>15 – 28</td>
<td>25</td>
<td>300</td>
<td>Toxic, flammable</td>
</tr>
<tr>
<td>H₂</td>
<td>-434</td>
<td>-423</td>
<td>4 – 75</td>
<td></td>
<td></td>
<td>Asphyxiant, flammable</td>
</tr>
<tr>
<td>SiH₄</td>
<td>-185</td>
<td>-112</td>
<td>Pyrophoric</td>
<td>5</td>
<td>Not est.</td>
<td>Highly toxic, pyrophoric</td>
</tr>
<tr>
<td>Si₂H₆</td>
<td>-206</td>
<td>+7</td>
<td>Pyrophoric</td>
<td>5</td>
<td>Not est.</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>PH₃</td>
<td>-133</td>
<td>-88</td>
<td>1% – ?</td>
<td>0.3</td>
<td>50</td>
<td>Highly toxic, pyrophoric</td>
</tr>
<tr>
<td>AsH₃</td>
<td>-116</td>
<td>-55</td>
<td>4.5 – 64</td>
<td>0.05</td>
<td>3</td>
<td>Highly toxic, flammable</td>
</tr>
<tr>
<td>GeH₄</td>
<td>-165</td>
<td>-89</td>
<td>? – &gt; 98%</td>
<td>0.2</td>
<td>Not est.</td>
<td>Highly toxic, flammable</td>
</tr>
<tr>
<td>TMI (trimethyl indium)</td>
<td>+88</td>
<td>+134</td>
<td>Pyrophoric</td>
<td>0.1</td>
<td>Not est.</td>
<td>Highly toxic, pyrophoric</td>
</tr>
<tr>
<td>TMGa (trimethyl gallium)</td>
<td>-16</td>
<td>+57</td>
<td>Pyrophoric</td>
<td>Not est.</td>
<td>Not est.</td>
<td>Highly toxic, pyrophoric</td>
</tr>
<tr>
<td>TMAs (trimethyl arsenic)</td>
<td>+15</td>
<td>+125</td>
<td>Pyrophoric</td>
<td>0.2</td>
<td>Not est.</td>
<td>Highly toxic, pyrophoric</td>
</tr>
<tr>
<td>TMA (trimethyl antimony)</td>
<td>-88</td>
<td>+80</td>
<td>Pyrophoric</td>
<td>0.05</td>
<td>Not est.</td>
<td>Highly toxic, pyrophoric</td>
</tr>
</tbody>
</table>

Note: TMI, TMGa, TMAs and TMA are a class of compounds known as “metal organics”
Job safety analyses (JSA), by a cross-functional team of process engineers, maintenance technicians and safety professionals, should be used to generate safe operating procedures for all activities utilising hazardous chemicals. In compound semiconductor operations, a JSA should be performed for maintenance and decontamination on epitaxial deposition (whether vapour phase or molecular beam), plasma etching, backgrinding and sawing and point of use abatement equipment. Unique hazards that these procedures should attend to are prevention of fires from phosphorus collected in cold traps, arsenic and phosphorus particles control, and halogens ventilation.

The process safety management (PSM) program is designed to prevent the catastrophic release of chemicals resulting in injuries to employees. The elements of this program include employee participation plan, documentation of process safety information, process hazard analyses, written operating procedures, employee training, contractor management, pre-start-up safety review, mechanical integrity plan, hot work permits, management of change procedures, incident investigation, emergency response plan, and compliance audits. Ammonia, arsine, chlorine, diborane, hydrochloric acid, nitric acid, nitrogen trifluoride, ozone, and phosphine are listed chemicals. OSHA also defines training, organisation and PPE requirements for hazardous waste handling and emergency response operations.

The Uniform Fire and Building Codes, International Fire Code and National Fire Protection Association (NFPA) 318 (and certainly many other model codes and standards) have specific requirements for the construction, fire suppression, gas detection and alarming, and chemical storage and use of semiconductor facilities. For example, the 1997 Uniform Fire Code (UFC) contains Article 51, Semiconductor Fabrication Facilities requiring the special construction requirements for Group H, Division 6 Occupancies. Article 51 calls for unobstructed suppression of hazardous production materials (HPM) baths on workstations of combustible

<table>
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<tr>
<th>Arsenic Treatment Technology</th>
<th>Process Description</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| Iron co-precipitation       | Dissolved and particulate arsenic adsorbed using ferric chloride, hydroxide or sulfate. Unit operations include coagulation, sedimentation and filtration into non-hazardous sludge | • pH can affect efficiency  
• Filtration step subject to upset |
| Adsorption media            | Dissolved and particulate arsenic adsorbed onto granular media including metal matrices and ferric hydroxide | • Generally more expensive than iron co-precipitation  
• Suspended solids can cause clogging |
| Activated alumina           | Dissolved arsenic adsorbed onto powdered media | • Fluoride, chloride, and sulfate may compete for adsorption sites  
• Regenerations may be incomplete  
• Suspended solids can cause clogging |
| Lime Softening              | Dissolved and particulate arsenic adsorbed at high pH using calcium carbonate | • Semiconductor waste streams generally at low pH  
• High chemical use |
| Membrane filtration         | Dissolved and particulate arsenic removed using ultrafilters, nanofilters or reverse osmosis membranes | • More expensive than co-precipitation/adsorption technologies |
| Ion exchange                | Dissolved arsenic adsorbed onto cation exchange resin | • Fluoride, chloride, and sulfate may compete for adsorption sites  
• Regenerations incomplete resulting in need to replace media  
• Suspended solids can cause clogging |
construction. Catastrophic releases of toxic gas must be treated to less than one-half of the immediately dangerous to life and health (IDLH) concentration. The limitations for pyrophoric solids and liquids, such as metal organics used in vapour phase epitaxial deposition, are one pound each within the factory.

Because of the toxic nature of many air emissions from compound semiconductor facilities, protection of facility personnel from air intake entrainment should be provided as recommended by the Fundamentals Standard of the American Society of Heating, Refrigeration and Air Conditioning Engineers (ASHRAE).

**OTHER EHS CHALLENGES**

There are also many pending regulations and standards that will affect the compound semiconductor industry. As mentioned previously, in the United States the EPA is moving to decrease arsenic discharge limits for industrial waste water and prohibit the use of PFOS. Many companies in the silicon oxide segment of the industry have signed a Memorandum of Understanding with the EPA for the reduction of perfluorocompound emissions, which are implicated in global warming. There is potential that these reductions will become mandated for all of the industry through air permits.

New ergonomics rules are expected to be re-promulgated by OSHA. The job tasks of technicians performing repetitive motions may have to be modified to comply with these rules.

On the state and local level, communities with compound semiconductor operations are likely to adopt the Hazardous Materials Ordinance (HMO), which is codified in UFC Article 80. This ordinance requires detailed tracking and reporting to the local fire department of chemical storage at semiconductor and other facilities. In addition, semiconductor facilities with chemicals approaching or above RMP thresholds are obligated to participate in the annual emergency planning activities of their LEPC.

Compared to newer generation silicon oxide semiconductor factories, most compound semiconductor operations are relatively small, allowing their location proximate to neighbourhoods. Environmental justice issues, which can be reported to and acted upon by EPA as part of their 1995 Environmental Justice Strategy, are likely to surface as communities become aware of the chemical transportation and accidental release hazards these facilities pose.

In Europe, the CE Mark and Machine Directives are required of all manufacturing equipment. Complying with these requirements can be difficult when shipping or transferring manufacturing equipment from the United States to Europe.

**EQUIPMENT-RELATED ISSUES**

Equipment purchase agreements are usually the vehicle used to notify equipment suppliers of regulations and standards that must be complied with. Compliance with Semiconductor Equipment and Materials International (SEMI) Safety Guidelines and many other regulatory documents, as well as many semiconductor manufacturers, is now a common requirement. In addition, many semiconductor manufacturers are requiring that equipment undergo design for environment (DFE) and life cycle assessments (LCA).

New ergonomics rules are expected to be re-promulgated by OSHA. The job tasks of technicians performing repetitive motions may have to be modified to comply with these rules.

**FACILITY-RELATED ISSUES**

Many communities in the United States do not, or soon will not, attain CAA National Ambient Air Quality Standards (NAAQS) for nitrogen oxides (NOx). Semiconductor operations within such communities can expect lower thresholds for restrictive Title V permits and the implementation of volatile organic compounds (VOC) and NOx emissions reductions programs, such as mandatory employee trip reductions.

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### Table 3. Arsenic and Phosphine Air Emissions Abatement Technologies

<table>
<thead>
<tr>
<th>Hydride Abatement Technology</th>
<th>Process Description</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbent media</td>
<td>Various metal matrices chemisorb hydride, sometimes with catalytic oxidation</td>
<td>• Results in solid waste</td>
</tr>
<tr>
<td>Combustion devices</td>
<td>Natural gas or hydrogen fires oxidise hydride</td>
<td>• Can produce small toxic oxide particles that are strictly regulated</td>
</tr>
<tr>
<td>Water scrubbers using potassium permanganate or sodium hypochlorite and sodium hydroxide</td>
<td>Packed bed scrubbers, utilising oxidising water, converts and absorbs arsenic</td>
<td>• Arsenic contaminated waste water, which is strictly regulated, is generated • Chemical feed often difficult to control accurately for maximum efficiency</td>
</tr>
</tbody>
</table>
Recently, semiconductor manufacturers are being forced to consider natural resource conservation. Partly because some communities have begun asking large users to reduce power demand during times of extreme temperatures, energy conservation is being implemented at the equipment and facility utility level. Energy conservation results in a reduction of fuels used by energy utilities, thereby lowering emissions of the global warming compound carbon dioxide and criteria pollutants. Since many semiconductor facilities are located in arid areas, water conservation, which is composed of use reduction, reclaim and recycle, is also being implemented. Of course, another benefit of resource conservation is the associated reduction in utilities cost per unit production.

Best practices for gas monitoring and alarm systems design are constantly changing. Whether to monitor for the process gases or their by-products, what concentrations should be used for warning and alarm, and where to locate sensors continue to be debated. While the silicon oxide segment of the industry generally demonstrates air emissions abatement system performance through parametric monitoring, the compound semiconductor segment often installs emissions monitoring systems to ensure that highly toxic gases are being properly abated.

To ensure against purchasing or selling property with historical environmental contamination, the current best practice for real estate transactions now requires the completion of an environmental due diligence report.

**CUSTOMER-RELATED ISSUES**

Semiconductor products customers worldwide have begun demanding that the semiconductor industry implement and demonstrate best practices for EHS programs. The industry has responded by instituting EHS management systems, typically in compliance with or modelled after the International Organisation for Standardisation (ISO) 14000 series of environmental management standards.

Customers are also becoming more interested in ensuring that semiconductor products do not contain banned substances and are recyclable, because of product take-back requirements in some nations. Accordingly, product content surveys, that can be exceedingly difficult to complete, are becoming ever more common.

The European Information & Communication Technology Industry Association (EICTA) and Electronic Industries Alliance (EIA) have developed lists of common reportable materials, and standardised solicitation and reporting procedures.

**EMERGING TECHNOLOGIES FOR EHS**

Several new technologies are commercially available allowing safer storage and delivery of toxic hydrides utilised in compound semiconductor manufacturing. Sub-atmospheric cylinders incorporating adsorbent media maintain cylinder pressures at near or below atmospheric pressure. Vacuum-actuated cylinders utilise pressure regulators inside of the cylinder that lower maximum delivery pressure to below the internal cylinder pressure. Source generation of hydrides from solid sources dramatically lowers the storage at any one time.

New exhaust emission abatement technologies provide improved removal efficiency for continuous emissions and catastrophic releases. Integrated combustion and scrubbing units are available for point-of-use abatement of epitaxial deposition process exhaust, which can contain flammable, pyrophoric and corrosive gases. Canister-type resin adsorber systems are available for removal of hydrides from process exhaust. Roof mounted resin adsorbers can treat catastrophic releases of hydride gases.

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**Table 4. Semiconductor EHS Support Organisations**

<table>
<thead>
<tr>
<th>Organisation</th>
<th>Membership</th>
<th>Activities</th>
<th>Internet URL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semiconductor Environmental, Safety and Health Association (SESHA) Compound Semiconductor Forum</td>
<td>EHS personnel, process and equipment engineers manufacturing and support equipment suppliers, chemical suppliers, and researchers</td>
<td>Provides professional networking and education on compound semiconductor (CS) EHS issues</td>
<td><a href="http://www.seshaoline.org">www.seshaoline.org</a></td>
</tr>
<tr>
<td>SEMI EHS Committee</td>
<td>Equipment suppliers, semiconductor manufacturers and “third party” equipment reviewers</td>
<td>Develops EHS standards and guidelines for semiconductor equipment</td>
<td><a href="http://www.semi.com">www.semi.com</a></td>
</tr>
<tr>
<td>International SEMATECH (ISMT) Equipment EHS Working Group</td>
<td>ISMT member company representatives</td>
<td>Performs selected EHS projects</td>
<td><a href="http://www.sematech.org">www.sematech.org</a></td>
</tr>
<tr>
<td>Air &amp; Waste Management Association (A&amp;WMA)</td>
<td>Environmental technical and legal professionals</td>
<td>Provides education and professional networking opportunities</td>
<td><a href="http://www.awma.org">www.awma.org</a></td>
</tr>
<tr>
<td>Semiconductor Industry Association (SIA)</td>
<td>SIA member company representatives</td>
<td>Represents the semiconductor industry to Federal agencies</td>
<td><a href="http://www.semichips.org">www.semichips.org</a></td>
</tr>
</tbody>
</table>
NOx emissions from natural-gas-fired combustion sources, primarily boilers, can be reduced from over 100 ppm to 30 ppm and lower using variations of oxygen trim technology. Process-logic-based combustion management systems (CMS) vary combustion air and flue gas recirculation feed rates as functions of heat demand. Some of these technologies are also effective at lowering CO emissions.

Several new water treatment technologies have application to compound semiconductor waste water discharges. Metal matrix adsorption media have been proposed in place of iron co-precipitation for arsenic removal. Electrodeionisation and continuously cleaned membrane systems, utilising vibration, have application both in waste water treatment and for replacing or supplementing ion exchange and reverse osmosis systems in ultra-pure water production, respectively.

**RESOURCE RECOVERY FOR GALLIUM**

Gallium is a limited resource that is produced as a by-product of aluminium and zinc processing. Presently, demand exceeds new production, necessitating resource recovery. Recyclers in Germany, Japan, the United Kingdom, Canada and the United States are capable of reclaiming gallium from waste semiconductor wafers and chips, as well as from other waste streams including the sludge produced from arsenic treatment of waste water. Gold and other precious metals can also be recovered prior to recycling.

**EHS SUPPORT ORGANISATIONS**

There are a variety of professional and industry organisations available to assist EHS professionals in the semiconductor industry. Table 4 provides a listing of these organisations and how to contact them.

**ABOUT THE AUTHOR**

Mr. Davis’ present position is Principal Staff Engineer for Motorola Semiconductor Products Sector’s Environmental, Health and Safety Department’s Technology and Engineering Support Group. Since 1990, he has served in a wide range of operational safety and environmental compliance positions, represented Motorola on International SEMATECH project working groups and SEMI’s EHS Committee, and managed numerous special projects. Recent projects have been related to treatment of air emissions and water discharges, water and energy conservation, alternative code compliance, and system and fire risk assessments. He has served as chair of the Travis County Local Emergency Planning Committee since 1995 and as an officer of the Air & Waste Management Association Central Texas Chapter since 1998. He also recently founded the SESHA Compound Semiconductor EHS Forum. Prior to joining Motorola, he was employed as a project engineer in the natural gas service industry and as a hazardous materials engineer by the City of Austin Fire Department. He has a BS in chemical engineering from the University of Texas and an MS in hazardous waste management from National Technological University. He has been a registered professional engineer in Texas since 1991.