Unique Industrial Hygiene Aspects in Gallium Arsenide Device Manufacturing Facilities

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Outline

• Gallium arsenide overview
• Various operations – IH issues
  – MOCVD
  – MBE
  – Plasma Etch
  – Saw and Grind
  – Wastewater treatment
  – Equipment decontamination
• Air and wipe sampling strategies
• Training
• OSHA’s inorganic arsenic standard
• Summary
General Gallium Arsenide (GaAs) Information

- Part of the “III-V” or compound semiconductor family
- Fused 48% Gallium and 52% Arsenic in wafer form
- Typical GaAs fabs use 4” or 6” wafers in manufacturing
- Wafers are stable at NTP
- GaAs has better semiconducting properties for certain operations over silicon substrates—different product applications especially wireless & optical communications
General Gallium Arsenide (GaAs) Information

- Similar equipment used in processing
- Some differences in processing techniques/applications
- Wastewater treatment (arsenic) is a major environmental concern. Local limits for device manufacturers vary. Wafer growers have higher limits
- Discussion of lowering drinking water limit to 50 ppb or less
- Hazardous waste considerations due to arsenic content of wafers
- Crystal growing will not be discussed in this presentation
Metalorganic Chemical Vapor Deposition (MOCVD) - General

• Used to grow thin epitaxial layers on GaAs substrates
• Many fabs contract EPI growth to foundry operations
• Arsine (AsH3) and Phosphine (PH3) gas are used
• Several pyrophoric/toxic metalorganics used as well: triethylgallium, triethyl aluminum, triethylindium, others
• Potential inclusion in OSHA 1910. 119: Process Safety Management (PSM) of Highly Hazardous Chemicals (Threshold Quantity: 100 lbs for AsH3 and PH3)
• Frequent maintenance on internal reactor and abatement systems is needed
Metalorganic Chemical Vapor Deposition (MOCVD)- Maintenance

- As and P particle trap removal
- As and P trap cleaning
- Hydride gas abatement system maintenance
- Hydride gas delivery and changeout
- Preventative maintenance
- Reactor chamber access and process lines
Metalorganic Chemical Vapor Deposition (MOCVD) - Particle Traps

- Particle traps need frequent exchange and clean-out
- High [As] and white [P] are present and are in fine particulate and dry form
- Air sampling: Direct reading instruments and OSHA compliance
- Spill containment (subfloor covers)
- Phosphorus fire response
- Respiratory protection and PPE
- Special training
Metalorganic Chemical Vapor Deposition - Phosphorus Particle Traps

- Phosphorus (P) cold traps filter undeposited P before hitting the hydride abatement systems. P is formed from PH3.
- Clogging of trap exhaust lines/valves is a concern.
- P is in the white allotropic form, thus is pyrophoric and toxic (PEL = 0.1 mg/m3).
- A full trap can have up to several pounds of concentrated white P.
- P ignition will create toxic phosphorus oxides. PH3 presence is also likely.
- P trap cleanout requires a special cleaning and maintenance area with proper safety systems. Copper sulfate recirculators are common.
- Pyrophoric nature requires flame retardant PPE and air line respiratory protection.
Metalorganic Chemical Vapor Deposition - Arsenic Trap Maintenance

- Cold traps filter undeposited As before hitting hydride abatement systems
- Full trap can have up to several pounds of concentrated As in dried and fine particulate form
- Cleanout may require soaking in mild chemical solution. AsH3 or other toxic As oxides can be formed
- Soaking/cleaning must take place in a balanced chemical hood or glove box. Introduces a significant slug of As to wastewater treatment system
- Respiratory protection and PPE
- Special training
Molecular Beam Epitaxy (MBE) - Process

- Used to grow ultra-thin epitaxial crystals on substrate
- Process uses very high vacuum and a furnace heating element to volatilize source materials
- Typically uses solid P, In, As, Ga source materials
- Increasing popularity in manufacturing environments
- Several advantages over MOCVD
Molecular Beam Epitaxy-General Maintenance IH Concerns

- Reactor access
- Potential hydride formation
- White phosphorus (P) traps
- Air sampling & PPE
- Local exhaust ventilation (careful with material of construction and P handling)
- Area contaminant control
Molecular Beam Epitaxy-
Trap Maintenance IH Concerns

• White phosphorus (P) trap maintenance
• Pyrophoric material
• Potential Phosphine and Phosphorus oxidation concerns
• Air sampling and PPE
• Special training
Plasma Etch - General

- Polymer or metal etch processes
- Source via etch is also common in GaAs manufacturing
- Similar gases used as found in Silicon fabs: BCl3, Cl2, O2, perfluorocarbons, inerts
- Source via etches directly into GaAs substrate through backside of wafer
- Etch chamber maintenance cleans are common and frequent
Plasma Etch - Maintenance

- Source via etch is largest IH concern since [As] is present in the chamber as a byproduct
- Wet cleans typically use DI water to physically wipe internal chamber
- Opening chamber (humidity) and application of DI water will liberate chlorinated, fluorinated, and arsenic compounds (arsine generation possible)
- Local exhaust is necessary as exposure control
- Extensive air sampling to document exposure potential to typical etch clean gases as well as arsenic compounds (including arsine)
Plasma Etch - Maintenance

- Point of use water scrubbers will be contaminated with arsenic compounds
- Need to review preventative maintenance practices on scrubbers
- Clogging is a typical problem and may require access/flange replacement in tight spots
- Clean or soak flanges, etc. in a chemical exhaust hood (halogenated compounds are concentrated and very reactive). Ensure water is disposed of properly
- Local exhaust ventilation should be used (leave scrubber exhaust on!)
- Take air samples during maintenance activities
- PPE & Training
Saw Operations- General

- Centrifugal saws cut wafers into die
- Large quantities of DI water are used as a blade cooling mechanism as well as a particle carrier fluid
- Typically, chemical additives are not used in saw operations
- GaAs particulates generated are typically >1 um with a bulk weight distribution of >5 um
- Saws generate ~20-25% of arsenic load in waste stream
Saw Operations- Maintenance

- Preventative maintenance requires access to contaminated areas of saws
- Saw blade exchange, chuck replacement, and general cleaning normally part of maintenance
- Dried arsenic particles of greatest concern for exposure
- Air and wipe sampling strategy needed to characterize exposure potential during maintenance AND housekeeping

- PPE
- Training
Wafer Backgrind - General

- Centrifugal ceramics physically grind the backside of wafers to reduce thickness
- Different devices require different wafer thickness
- Like saws, large quantities of DI water are used to cool rotating ceramics as well as a particle carrier fluid
- Typically, chemical additives are not used in GaAs saw operations
- GaAs particulates are finer than saws with <3 um particle size
- Grinders generate ~70% of arsenic load in waste stream
Wafer Backgrind- Maintenance

- Like saws, preventative maintenance requires access to contaminated areas of grinders
- Ceramic exchange, chuck replacement, and general cleaning normally part of maintenance
- Technicians have direct contact with large concentrations of GaAs sludge
- Air and wipe sampling strategy needed to characterize exposure potential during maintenance AND to monitor housekeeping
- PPE
- Training
Arsenic Wastewater Treatment Systems - General

• Wastewater treatment systems used to extract [As] out waste stream

• Ferric-Chloride most popular method used

• High chemical usage: Ferric chloride inject, pH adjust (H2SO4, NaOH), coagulant additives, antibacterial chemicals

• Can be high concentrations of [As] in wastewater or other parts of system

• Industrial centrifuges used to collect bulk of GaAs particles before hitting treatment system
Arsenic Wastewater Treatment Systems - Filter Press

- Filter plates require frequent cleaning of arsenic laden ferric hydroxide cake

- “Filter Cake” is ionically bound As in a ferric hydroxide matrix

- Filter cake can have up to several thousand ppm of [As] in the bound matrix

- PPE

- Training

- Housekeeping
Arsenic Wastewater Treatment Systems - Centrifuge

- Industrial sized centrifuge used to remove suspended GaAs particles before hitting the wastewater treatment system
- Large concentration of GaAs collected over time
- Removal of collection drums and system maintenance
- Dried [As] a concern
- PPE, Training, & Labeling
Process Equipment Decontamination

• Must consider presence of As, AsH3, P, and PH3 in decommissioned tools and abatement equipment

• Water from equipment decon may have high [As]

• Decontamination chemicals must be considered so as not to create toxic hydrides or oxide gases. Green Windex has been effective

• Decon operations should be performed on designated hazardous decontamination pads

• Air sampling

• PPE

• Training
Air Sampling Strategy

• Arsenic requires full shift air sampling per OSHA regulations

• NIOSH 7901 OR 7300 (arsenic)

• Proposed arsine TLV reduction from 50 ppb to 3 ppb by ACGIH (NIOSH 6001)

• Since largest concern is with maintenance activities, it’s a good idea to collect both short-term AND full shift samples (one for compliance and one for characterization)

• Important to have a re-sample policy or plan

• Areas of arsenic/arsine potential: MOCVD, MBE, Saw/Grinder, Dry Etch, Decontamination Activities, Wastewater Treatment.
Wipe Sampling Strategy

• A housekeeping plan is required under OSHA’s inorganic arsenic standard

• Should have a wipe sampling strategy or schedule to monitor adherence to that housekeeping plan

• No OSHA standard exists for arsenic contamination

• Housing and Urban Development (HUD) standard for lead can be used as a reference for contamination: 100ug/ft² for floors, 500 ug/ft² for window sills and 800 ug/ft² for window wells
GaAs Fab Training & Information

- All fab operators should have basic orientation on GaAs
- Technicians or engineers performing maintenance activities should have detailed training on properties and toxicology of As
- Specific training on MOCVD system including trap maintenance and handling
- GaAs fab jobs that should have additional training: saw/grinder technicians, MOCVD operators/technicians/engineers, wastewater treatment technicians
OSHA’s Inorganic Arsenic Standard

- 1910.1018 Inorganic Arsenic (Arsine exposure not applicable)
- Initial 8-hour air sampling on every shift determines applicability of several provisions of standard
- Exceeding the PEL (0.01 mg/m3) requires the following provisions:
  - Establishment and demarcation of a regulated area
  - Notification to OSHA of regulated area, summary of operations, and plans to reduce employee exposures
  - Written program with engineering plans/studies, monitoring schedule, to reduce exposures to below PEL through engineering and work controls
  - Additional air sampling required every 6 months
OSHA’s Inorganic Arsenic Standard

• Exceeding the PEL (0.01 mg/m3) requires the following provisions. Some of the provisions may apply to exceeding the action level (0.005 mg/m3):
  - Respiratory protection requirements dependent on air sampling results
  - Establishment of hygiene facilities including change rooms, showers, lavatories, and lunch rooms
  - Medical surveillance and training
OSHA’s Inorganic Arsenic Standard

- Initial air monitoring for every shift. Results must be below the action level (0.005 mg.m³).
- Additional monitoring required upon change in operations which may result in new or additional exposure to arsenic.
- Employee notification within 5 days of monitoring results.
- A written housekeeping and maintenance plan to minimize arsenic dispersion.
- Specific verbiage on labeling arsenic shipping or storage containers (not applicable to GaAs wafers).
OSHA’s Inorganic Arsenic Standard

- The following provisions apply to ALL potential inorganic arsenic exposures:
  - Appropriate, freshly laundered (or new) PPE for employees with skin exposure potential
  - Inform laundering services (in writing) of potentially harmful and carcinogenic effects of exposure to inorganic arsenic
  - Storage of PPE to prevent dispersion of inorganic arsenic
  - Must ensure contaminated PPE/clothing is specifically labeled with proper verbiage according to the standard
  - Floors may not cleaned by compressed air, shoveling, or brushing. Vacuums may be used for cleaning but must minimize reentry of inorganic arsenic into the workplace (HEPA)
Summary

- Maintenance activities in GaAs fabs = largest exposure potential
- AsH3/PH3 usage and presence of [As] and [P] are the largest IH concern and primary difference between Silicon and GaAs fabs
- MOCVD operations have additional concerns due to PH3 use
- MOCVD and MBE have white P as a hazardous byproduct
- Main areas of concern include: Saws/Grinders, MOCVD, MBE, Wastewater Treatment, Decontamination, and Dry Etch
- Compliance with OSHA’s arsenic standard must be considered and documented. Air sample all potential exposures
- Special and detailed training for individuals performing maintenance should be given and documented as a supplement to general hazard communication training