

Characterization of Arsenic Rich Waste Slurries Generated During Gallium Arsenide Wafer Lapping and Polishing.

¹ Keith W. Torrance, ¹Helen E. Keenan, ²Jan Sefcik, & ³Andrew Hursthouse.

¹ David Livingstone Centre for Sustainability, University of Strathclyde, Glasgow, UK;

²Dept. of Chemical Engineering, University of Strathclyde, Glasgow, UK

³ University of the West of Scotland, Paisley, UK.

keith.torrance@strath.ac.uk

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Abstract

The toxicology of gallium arsenide is well established; it is classified by the state of California as a known carcinogen. Consequently, environmental aspects of GaAs wafer manufacture are coming under greater scrutiny, with the cost of waste disposal becoming an economic issue for fabs operating under this jurisdiction. It is estimated that 85% of a GaAs boule is lost during manufacturing and device packaging, which usually ends up land filled as hazardous waste. This percentage is likely to increase as final wafer thickness is reduced to improve thermal dissipation. GaAs wafer backthinning and polishing generates waste slurries that are contaminated by arsenic and must be disposed of as hazardous waste. Although GaAs is largely insoluble in H₂O, it is readily oxidized to soluble oxides and hydroxides, especially during chemo-mechanical polishing. Further, the valency state of the arsenic species determines the toxicity of effluent. Waste slurries from three sources were studied by ICP-MS and ICP-OES analysis to determine the amount of arsenic in the supernate and the form of the arsenic species. This data was related to mechanical lapping processes, such as the size distribution of particles in the slurry, and to the oxidation chemistry of the polishing processes. The analytical results provide guidance as to the most effective strategy to minimize the environmental impact of slurries produced during wafer thinning and polishing.

EXPERIMENTAL

Waste slurries were collected from three companies working with single crystal gallium arsenide substrates.

These represented the main types of waste flow; slurries of GaAs particles from cutting and grinding operations, wafer lapping slurries and chemical polishing slurries. These were compared to slurries prepared under laboratory conditions. The characteristics of each type are shown in Table 1.

TABLE 1
CLASSIFICATION OF SLURRY TYPES

Type	Source	Characteristics	pH	GaAs g l ⁻¹
Grinding slurry	Grinding of boules, wafering and dicing.	Clear solution with visible GaAs particles and surfactant.	7.0	0.25 - 1.25
Lapping slurry	Wafer back thinning.	Grey slurry of alumina and fine GaAs particles	8.0	0.45 - 1.75
Polishing slurry	Prime wafer polishing & backside polishing.	Clear solution with alumina & SiO ₂ fines. May be alkaline or acidic.	10 - 11 6.0	1.25 - 2.65

Potential hazards associated with GaAs wafer fabrication were first brought to the attention of the industry by NIOSH in 1987, following studies on *in vitro* solubility and toxicity by Webb et al (1984). This recognized the potential hazard from airborne GaAs particles and recommended that proper handling policies for GaAs be developed and that cutting, grinding and polishing be done in a wet medium to minimize the

generation of particulates. Jones, Sheehy et al (1988) expanded this work to inspect three GaAs fabs and identified areas of concern in crystal growth. At the time of these papers it was common for crystal growth, wafering and device fabrication to be carried out at a single site; the industry has since evolved to a well-defined supply chain with a small number of companies supplying all the substrate material. Other studies (Peterson, 2000; Jadvar et al 1991, Fayter, 1996) looked at methods to minimize and treat arsenic waste. It has been the practice in most semiconductor fabs to collect all the lapping and polishing waste to have it disposed of by an approved contractor into a landfill authorized to accept hazardous waste. Some reclamation of gallium is possible.

METHODOLOGY

Waste slurries were first separated into solids and the supernate by centrifuge. Three analytical techniques were used to determine the concentration of arsenic within the liquid phase. The simplest method employs a Hach [9] field test kit designed for measurement of arsenic in groundwater and uses indicator strips to estimate arsenic content within the range 0 – 500 ppb. This was found to be effective method to screen the samples for later ICP-MS and voltammetric analysis.

The solid phase of the lapping slurry was inspected using SEM and the particle size distribution estimated using laser scattering. In contrast to the larger 9 μm alumina abrasive particles, most of the GaAs particles are sub-micron with a mean diameter of around 0.4 μm in diameter and are highly angular as shown in Figure 1.

RESULTS AND DISCUSSION

Arsenic content of the twelve sample slurries is shown in Figure 2. Samples will also be analysed by ICP-MS. Not surprisingly, the raw polishing slurries show the highest arsenic content (1000ppm+), which is consistent with an oxidizing chemical polish. The lapping slurries are consistent within a range of 10 – 100 ppm; the actual concentration will vary depending on the level of dilution during cleaning etc. This suggests that 2 – 5% of GaAs is dissolved in the carrier fluid during the lapping process. We suspect that this is related to the particle size distribution and surface area available for hydration and oxidation.

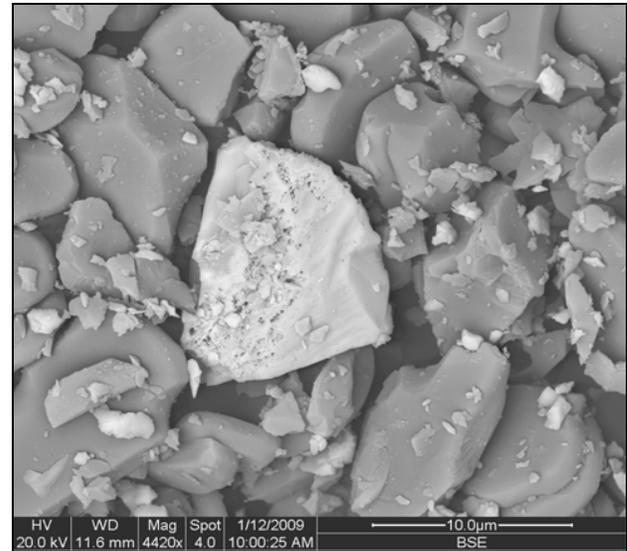


Figure 1: SEM photomicrograph of alumina lapping slurry with smaller GaAs fragments.

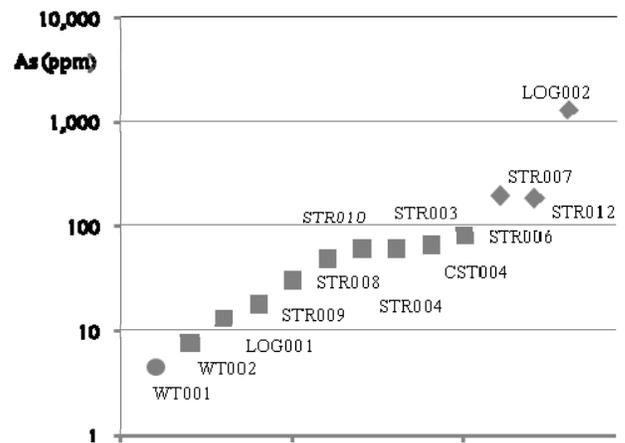


Figure 2: Arsenic content of waste slurries.

The lowest arsenic concentration is found in the waste stream from boule cutting and grinding. This slurry is characterized by a wider range of particle sizes, including some larger pieces (>50 μm) and contained a detergent-based lubricant. This larger size range may limit the surface area of GaAs available for oxidation. GaAs is not readily soluble in water. However, the oxidation product As₂O₃ is highly soluble and forms a thin film on freshly exposed GaAs faces.

CONCLUSIONS

Wafer thinning generates a relatively large volume of arsenic rich liquid waste. There are marked differences in the percentage of GaAs that goes into solution depending on the method used to thin the wafer, with polishing \geq lapping \geq grinding in terms of waste arsenic content.

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REFERENCES

- [1] DOMINGO, J. L.; CORBELLA, J. 1991. A review of the health hazards from Gallium Arsenide exposure. *Trace Elements in Medicine*, **8** (2), 56-64
- [2] FAYTER, RUSTY. 1996. *Wastewater recycling at Watkins-Johnson Company Building 5*. Internal publication. Palo Alto : Watkins-Johnston
- [3] JADVAR, REZA, MCCOY, BENJAMIN, FORD, BILL & GALT, GERRY. 1991. Recovery of Gallium and Arsenic from GaAs wafer manufacturing slurries. *Environmental Progress*. **10**(4) 278 - 281
- [4] PETERSON, JOEL 2000. Managing Arsenic in GaAs Fab Wastewater. *2000 IEEE/SEMI Advanced Semiconductor Manufacturing Conference*. 187 – 195
- [5] SHIRE, DOUGLAS B. 1994. Hazardous Waste Minimization in III-V Wafer Fabrication Processes. *IEEE Transactions on components, packaging, and manufacturing technology-part A*. December 1994. **17**. No. 4.
- [6] STURGILL, J. A; SWARTZBAUGH, J.T.; RANDALL, P.M. 2000. Pollution prevention in the semiconductor industry through recovery and recycling of gallium and arsenic from GaAs polishing wastes. *Clean Products and Processes*, **2** 18–27 Q Springer-Verlag 248 - 256
- [7] WEBB, D.R., SPIES, I.G. & CARTER, D.E. 1984. *In Vitro* solubility and *In Vivo* toxicity of Gallium Arsenide. *Toxicology and Applied Pharmacology* **76**, 96 – 104
- [8] WEBB, D.R., WILSON, S.E. & CARTER, D.E. 1985. Comparative pulmonary toxicity of Gallium Arsenide, Gallium (III) Oxide or Arsenic (III) Oxide Intratracheally Instilled into Rats. *Toxicology and Applied Pharmacology* **82** 405 - 416
- [9] HACH COMPANY, Loveland, CO, USA
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