Management of arsenic-rich waste streams in III-V foundries

Keith Torrance and Helen Keenan of the University of Strathclyde discuss safe practices for waste management associated with the grinding, lapping and polishing of gallium arsenide in the wafer thinning process.

Backside processing of gallium arsenide and other III–V semiconductors dictates that fabricated wafers are thinned from 625μm to less than 100μm to improve heat dissipation of the diced and packaged device.

Wafer grinding, lapping, polishing or a combination of processing methods is most commonly used in the fab to mechanically abrade material from the backside of the wafer. Grinding using a resin-bonded fixed diamond wheel is the preferred method for 100mm and larger substrates, but lapping is still used for lower-volume operations. The resulting waste stream is in the form of slurry, with solid GaAs and abrasive particles mixed with coolant that contains dissolved arsenic. In the USA, the State of California has recently classified GaAs as a known carcinogen and, under most legislative regimes, the waste streams from backthinning are classified as hazardous waste. This article seeks to explain the chemical and physical characteristics of this

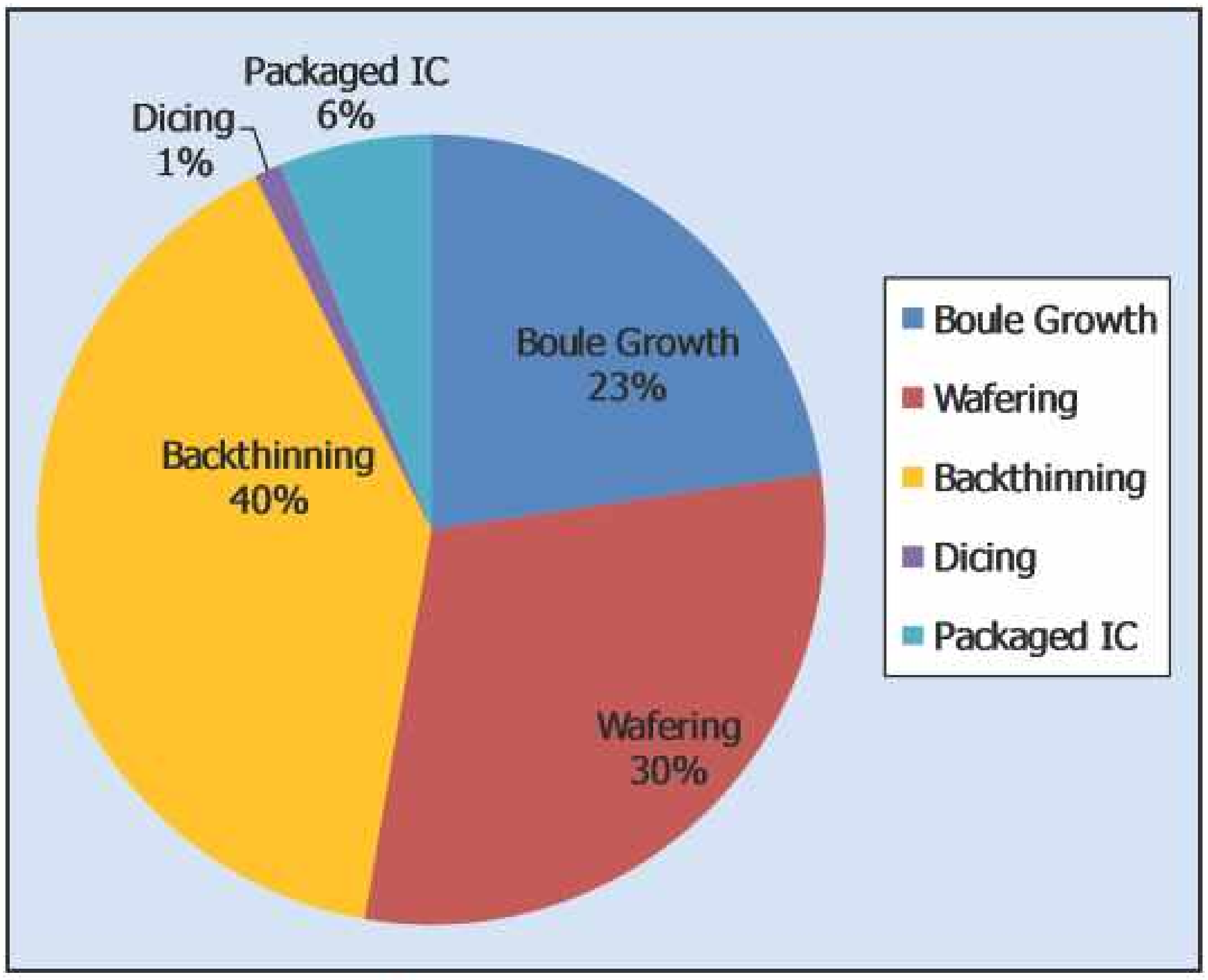

Figure 1. Material losses during processing from boule to packaged IC (without recycling).

Table 1. Characteristics of GaAs processing waste streams.

Type	Source	Characteristics	pH	Total GaAs*(gl^{-1})	Dissolved As (mgl^{-1})
Grinding slurry	Grinding of boules, wafering and dicing	Slurry with visible GaAs particles and surfactant	7.0	20–75	10
Lapping slurry	Wafer back lapping	Grey slurry of alumina and fine GaAs particles	8.0	20–30	20–90
Polishing slurry	Prime wafer polishing & backside polishing	Clear solution with alumina & SiO_2 particles. May be alkaline or acidic	10–11 6.0	3–5	1800–2400

* Solid GaAs particulates and dissolved material.

waste, the legislation that covers its safe disposal and to provide some guidance on safe practices for handling waste.

GaAs wafer processing is very inefficient in its use of substrate material. It can be calculated that up to 94% of a grown GaAs boule is potentially discarded during wafering and subsequent backthinning operations (Figure 1). Although some recycling of substrate material is possible, e.g. during boule growth, it is only economical to recover certain metals, such as gallium, from the waste. The residue is therefore further enriched in arsenic, and must be disposed of as hazardous waste, as there are limited uses for arsenic. Further, during thinning, a significant proportion of arsenic becomes soluble, so that any water used as a coolant or for cleaning is potentially contaminated.

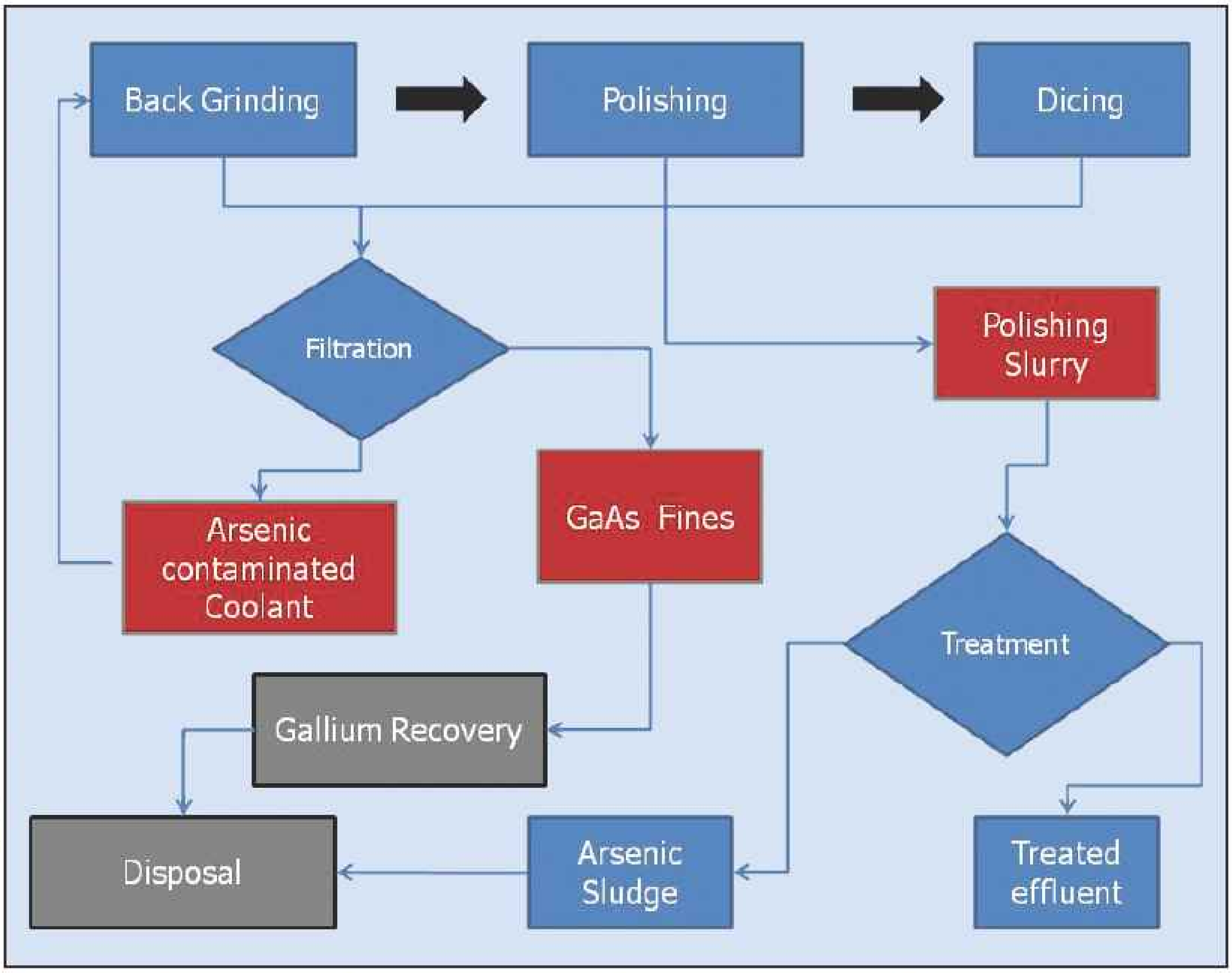

Figure 2. Gallium arsenide waste stream flow chart within a fab.

Arsenic is recognised as both a chronic and acute toxin; as little as 100mg of arsenic trioxide can be fatal. Arsenic can exist in several valence states, with the As^{-3} state (i.e. arsine gas) considered to be the most toxic [1], followed by As^{+3} valence state; inorganic arsenic compounds are more toxic than organic arsenic compounds. Millions of people worldwide, especially in West Bengal and Bangladesh, are at risk from chronic health problems associated with the consumption of groundwater that is naturally high in arsenic. Prolonged ingestion of arsenic results in higher incidences of keratosis, skin and bladder cancers. The World Health Organisation (WHO) has set a target maximum permissible level of $10\mu gl^{-1}$ arsenic in drinking water, although this level is exceeded in many parts of the world from natural sources.

The chemistry and physical characteristics of the main waste streams are shown in Table 1. Arsenic content is best determined using inductively coupled plasma mass spectrometry (ICP-MS), although there are a number of simple colourometric test kits that can be used to monitor the arsenic content of waste waters inexpensively.

Slurries from wafer grinding and dicing are most amenable to recycling as the solids can be removed by recirculating the coolant through a filter. Based on laboratory studies, typical arsenic concentrations in the coolant are less than $10mgl^{-1}$, although this is still above most permissible discharge standards. Lapping slurries have a higher dissolved arsenic content (up to $100mgl^{-1}$). Recycling of these slurries is complicated by the presence of aluminum oxide abrasive, reducing the average gallium content to about 5% (on a dry basis), which is close to the economical threshold for gallium recovery. Several firms (including Recapture Metals Ltd of Peterborough, Ontario, Canada) can reclaim gallium metal from waste slurries. Polishing slurries have a dissolved As content of about $2000mgl^{-1}$, as all the GaAs that is removed will be in soluble form from the strong oxidizing nature of GaAs polishing solutions.

In the European Union, disposal of hazardous waste is covered by the Waste Framework Directive (2006/12/EC) [2]. Arsenic-containing waste is considered hazardous above $5mgkg^{-1}$ and must be disposed of in solid form in a licensed hazardous landfill. It is no longer acceptable to co-dispose hazardous and non-hazardous waste in the EU, and there are a diminishing number of compliant landfills, which adds to the cost of disposal. Water is removed from the slurry by the waste contractor, usually by incineration. One further consideration is that the transport of hazardous waste to destinations outside the EU is tightly regulated, making shipment of waste to North America for recycling problematic.

Table 2. Hazards associated with GaAs processing waste streams.

Waste stream	Possible hazards	Hazard minimization
Solid particles as dust	Inhalation of dust.	Minimize dust generation, through wet processing. Ventilation and extraction of working area of grinders and saws. Store waste in liquid slurry form in a closed container. Wear protective clothing, mask and gloves.
Grinding, cutting and lapping waste slurries	Ingestion of GaAs. Dermal contact. Contamination of groundwater through improper disposal.	Treat waste streams as hazardous waste and dispose of according to local and national regulations. Wear protective clothing and gloves.
	Generation of arsine gas in waste container.	Avoid creating a reducing environment in waste slurry tank. Maintain low pH in waste slurry tank to avert microbial activity.
Polishing slurries.	Ingestion of arsenic.	Wear protective clothing and gloves.

In the USA, arsenic is one of eight metals regulated under the Resource Conservation and Recovery Act (RCRA), and waste with a leachable content — as determined by the Toxicity Characteristic Leaching Procedure (TCLP) [3] — of more than $5.0 mgl^{-1}$ is considered hazardous. Although this is a less onerous standard than the EU definition, most waste slurries from GaAs lapping and grinding are still classified as hazardous. The US Environmental Protection Agency (EPA) has set effluent discharge standards for the semiconductor industry, including a peak limit of $2.09 mgl^{-1}$ for arsenic and an average of $0.83 mgl^{-1}$ over 24 hours.

On 1 August 2008, GaAs was classed by the State of California as a material that is a known carcinogen (California Proposition, 65 OEHHA) [4]. It is also toxic by inhalation and ingestion [5]. Consequently, sludge that contains GaAs particulates must be treated as hazardous waste and semiconductor workers must be protected from exposure. The primary concern is the inhalation of particulates; a ceiling value of $2 \mu gm^{-3}$ is recommended by the US National Institute for Occupational Safety and Health (NIOSH)[6].

Under the 'polluter pays' principle that underlies European Union regulation, the generator of waste retains a responsibility for the final disposition of the waste and is responsible for ensuring that the contractor is in compliance with all pertinent regulation

Table 2 summarizes the potential hazards associated with the different waste streams, together with some handling recommendations. There are a number of treatment options to remove soluble arsenic from waste water and bring it within discharge limits.

Most importantly, waste should only be transported and disposed of by a contractor licensed to handle hazardous waste. Under the 'polluter pays' principle that underlies EU regulation, the generator of waste retains a responsibility for the final disposition of the waste and is responsible for ensuring that the contractor is in compliance with all pertinent regulation.

Although there have been only a few reported instances of arsenic pollution resulting from semiconductor manufacture[7], the onus is on semiconductor foundries to properly manage waste streams and ensure compliance with local and national legislation. ■

Authors: Keith W. Torrance and Helen E. Keenan, David Livingstone Centre for Sustainability, University of Strathclyde, Glasgow, UK.

References

1. Henke, Kevin (Ed.) ARSENIC: Environmental Chemistry, Health Threats and Waste Treatment (John Wiley & Sons: New York), 2009, p592
2. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32006L0012:EN:NOT
3. www.ehso.com/cssepa/TCLP.htm
4. State of California Office of Environmental Health Hazard Assessment. Safe Drinking Water and Toxic Enforcement Act (Proposition 65 List of Chemicals). 2009, Title 27 (Cal/EPA)
5. Flora, Swaran J. S. 2000 Possible Health Hazards Associated with the Use of Toxic Metals in Semiconductor Industries. J. Occup. Health, 42, 105–110
6. NIOSH Reducing the Potential Risk of Developing Cancer from Exposure to Gallium Arsenide in the Microelectronics Industry. DHHS Publication No. 88–100, 1987 (Cincinnati: NIOSH)
7. Chen, H. W. Gallium, Indium, and Arsenic Pollution of Groundwater from a Semiconductor Manufacturing Area of Taiwan. Bulletin of Environmental Contamination and Toxicology, 2007, 77, 289–296