GALLIUM ARSENIDE

1. Exposure Data

1.1 Chemical and physical data

1.1.1 *Nomenclature*

Chem. Abstr. Serv. Reg. No.: 1303-00-0
Deleted CAS Reg. No.: 12254-95-4, 106495-92-5, 116443-03-9, 385800-12-4
Chem. Abstr. Serv. Name: Gallium arsenide (GaAs)
IUPAC Systematic Name: Gallium arsenide
Synonyms: Gallium monoarsenide

1.1.2 *Molecular formula and relative molecular mass*

GaAs Relative molecular mass: 144.6

1.1.3 *Chemical and physical properties of the pure substance*

(*a*) *Description*: Grey, cubic crystals (Lide, 2003)
(*b*) *Melting-point*: 1238 °C (Lide, 2003)
(*c*) *Density*: 5.3176 g/cm^3 (Lide, 2003)
(*d*) *Solubility*: Insoluble in water (Wafer Technology Ltd, 1997); slightly soluble in 0.1 M phosphate buffer at pH 7.4 (Webb *et al*., 1984)
(*e*) *Stability*: Decomposes with evolution of arsenic vapour at temperatures above 480 °C (Wafer Technology Ltd, 1997)
(*f*) *Reactivity*: Reacts with strong acid reducing agents to produce arsine gas (Wafer Technology Ltd, 1997)

1.1.4 *Technical products and impurities*

Purity requirements for the raw materials used to produce gallium arsenide are stringent. For optoelectronic devices (light-emitting diodes (LEDs), laser diodes, photodetectors, solar cells), the gallium and arsenic must be at least 99.9999% pure; for integrated circuits, a purity of 99.99999% is required. These purity levels are referred to by several names: 99.9999%-pure gallium is often called 6-nines, 6N or optoelectronic grade, while 99.99999%-pure gallium is called 7-nines, 7N, semi-insulating (SI) or integrated circuit (IC) grade.

For 7N gallium, the total of the impurities must be < 100 μg/kg. In addition to the challenge of consistently producing material with such high purity, there are difficulties in detecting the small quantity of impurities. Certain impurities cause more problems than others during gallium arsenide production. Those of most concern are calcium, carbon, copper, iron, magnesium, manganese, nickel, selenium, silicon, sulfur, tellurium and tin. Generally, these elements should be present in concentrations < 1 μg/kg in both the gallium and the arsenic. Lead, mercury and zinc should be present in concentrations < 5 μg/kg. Although aluminum, chlorine and sodium are often present, the concentrations of each should be < 10 μg/kg (Kramer, 1988). Some companies have even more stringent requirements (Recapture Metals, 2003).

1.1.5 *Analysis*

The monitoring of occupational exposure to gallium arsenide can only be based on measurements of arsenic or gallium concentrations in workplace air or in human tissues or body fluids (biological monitoring), because there is no analytical method capable of measuring gallium arsenide per se in the above media.

(*a*) *Determination of gallium*

Monitoring of exposure to gallium arsenide by determination of gallium has so far not been used due to the limited availability of analytical methods with sufficiently low detection limits.

Instrumental neutron activation analysis (INAA) has been employed successfully for the determination of gallium in ambient air (Kucera *et al.*, 1999) and can therefore be used for the determination of gallium in workplace air. A newly developed Mist-UV sampling system coupled with ICP–MS analysis allows the determination of volatile gallium compounds in the atmosphere (Ito & Shooter, 2002).

Several methods have been designed and tested for the determination of gallium in biological materials, mainly in the analysis of spiked samples. These include spectrophotometry (Beltrán Lucena *et al.*, 1994), fluorescence spectrometry (Requena *et al.*, 1983; Afonso *et al*,. 1985; Ureña *et al.*, 1985; Ureña Pozo *et al.*, 1987; Cano Pavón *et al.*, 1988; Salgado *et al.*, 1988; Cano Pavón *et al.*, 1990; Sanchez Rojas & Cano Pavón, 1995), electrothermal AAS (Nakamura *et al.*, 1982; Ma *et al.*, 1999) and F-AAS with preconcentration (Anthemidis *et al.*, 2003).

Data on gallium concentrations in human tissues and body fluids are scarce. Scansetti (1992) reported a mean blood concentration in healthy donors of 3 μg/L.

(*b*) *Determination of arsenic*

Until now, only measurements of arsenic have been used for monitoring exposure to gallium arsenide because occupational exposure limits for arsenic have been established in many countries and the analytical methods available for its determination are more sensitive than those for gallium.

(i) *Workplace air monitoring*

Yamauchi *et al.* (1989) measured arsenic concentrations in air in gallium-arsenide plants using a method similar to those used to determine inorganic arsenic in workplace air (Hakala & Pyy, 1995; Jakubowski *et al.*, 1998; Apostoli *et al.*, 1999). Airborne respirable particulate matter is collected by drawing air into a stationary or personal sampler through a membrane filter made of polycarbonate, cellulose ester and/or teflon. The filter containing the collected air particulates is digested in various concentrated mineral acids (chlorhydric acid, nitric acid, sulfuric acid, perchloric acid) or a mixture thereof and the arsenic concentration in the digest is determined by hydride generation AAS (Hakala & Pyy, 1995; Jakubowski *et al.*, 1998) or ICP-MS (Apostoli *et al.*, 1999). Non-destructive determination of the arsenic content on a filter can also be achieved using INAA, with a detection limit of about 0.5 ng/m^3 (Kucera *et al.*, 1999).

(ii) *Biological monitoring*

Preliminary considerations

Biomonitoring of exposure to gallium arsenide by measuring arsenic in human tissues or body fluids has several limitations. Firstly, gallium arsenide has a low solubility and is poorly absorbed in the gastrointestinal tract, resulting in rapid elimination of the compound in the faeces (Webb *et al.*, 1984; Yamauchi *et al.*, 1986) (see also Section 4.1.2). Secondly, determining the total concentration of arsenic in body fluids, e.g. in urine, is not an optimum measure of occupational exposure to arsenic. Gallium arsenide is partly dissociated *in vivo* into inorganic arsenic and gallium (Webb *et al.*, 1984; Yamauchi *et al.*, 1986). Inorganic arsenic is methylated in the human body to monomethylarsonic acid (MMA^V) and dimethylarsinic acid (DMA^V), which are readily excreted in urine (Vahter, 2002). However, arsenic in seafood is present predominantly in the forms of arsenobetaine and arsenocholine, which do not undergo biotransformation and are also excreted in urine (Apostoli *et al.*, 1999; Vahter, 2002). Hence, the concentration of total arsenic in body fluids is dependent on the concentration and the species of dietary arsenic. Therefore, it is preferable to use speciation analysis in biomonitoring of arsenic exposure; alternatively, subjects enrolled in occupational health studies should refrain from consuming seafood for a couple of days before the analysis of their body fluids.

Similarly, determination of arsenic concentration in hair is associated with the problem of distinguishing external contamination from the endogenous content of arsenic in this tissue (Yamauchi *et al.*, 1989).

Analytical methods

Numerous methods (reviewed recently in IARC, 2004) are available for the determination of the total concentration of arsenic and its species in blood, serum, urine and other biological materials. The methods most commonly used include electrothermal AAS, AAS with hydride generation, ICP-AES, ICP-MS, atomic fluorescence spectrometry (AFS) and INAA. The advantages and shortcomings of these and other less frequently used techniques, such as spectrophotometric and electroanalytical methods, have been reviewed comprehensively (Burguera & Burguera, 1997; IARC, 2004). The analytical methods used for arsenic speciation are based on the combination of a powerful separation process and an adequate element-specific detection, using so-called hyphenated analytical techniques. The methods most frequently employed for separation and preconcentration involve solvent extraction, including solid-phase extraction (Yalcin & Le, 2001; Yu *et al.*, 2003), precipitation and coprecipitation, ion-exchange chromatography (IEC), capillary electrophoresis (Greschonig *et al.*, 1998), gas chromatography and high-performance liquid chromatography (HPLC). The element-specific detection is performed using the same analytical techniques as for determination of total arsenic. On-line coupling of some separation techniques, usually HPLC or IEC, with the most sensitive detection methods (AAS, AFS, ICP-AES, ICP-MS) is frequently used. A detection limit at the nanogram level has been achieved by AAS coupled with hydride generation before detection (Burguera & Burguera, 1997).

(iii) *Reference values for occupationally non-exposed populations*

Concentrations of total arsenic found in human blood, serum, plasma and urine have been reviewed (Iyengar *et al.*, 1978; Versieck & Cornelis, 1980; Heydorn, 1984; Iyengar & Woittiez, 1988). The data suggest that there are regional differences and short-term effects of dietary intake, especially seafood. After exclusion of values suspected of such variations, the following median reference values were given: whole blood, 5 μg/L (Iyengar & Woittiez, 1988); serum or plasma, 1–3.5 μg/L (Heydorn, 1984; Iyengar & Woittiez, 1988); and urine, 20 μg/L (Iyengar & Woittiez, 1988). The data available for the individual arsenic species are still insufficient to make reliable estimates of reference values, presumably because of methodological problems.

1.2 Production and use

1.2.1 *Production*

Gallium occurs in very small concentrations in many rocks and ores of other metals. Most gallium is produced as a by-product of processing bauxite, and the remainder is produced from zinc-processing residues. Only part of the gallium present in bauxite and zinc ores is recoverable, and the factors controlling the recovery are proprietary. Therefore, an estimate of current reserves cannot be made. The world bauxite reserve base is so large that much of it will not be mined for many decades; hence, most of the gallium in the bauxite reserve base cannot be considered to be available in the short term (Kramer, 2003).

Estimates of primary production of gallium in the world between 1995 and 2002 have varied between 35 and 100 tonnes. In 2003, about 64 tonnes were produced, with China, Germany, Japan and the Russian Federation being the major producers; countries with smaller output included Hungary, Kazakhstan, Slovakia and the Ukraine. Refined gallium production in 2003 was estimated to be about 83 tonnes, including some scrap refining. France was the largest producer of refined gallium, using crude gallium produced in Germany as feed material. Japan and the USA are two other large gallium-refining countries (Kramer, 1996–2004).

Demand for gallium in the USA in 2003 was satisfied by imports, mainly low-purity material from China, Kazakhstan and the Russian Federation and smaller amounts of high-purity material from France. In addition, in 2002, the USA imported an estimated 120 tonnes of doped and undoped gallium arsenide wafers, mainly from Finland, Germany, Italy and Japan (Kramer, 2002, 2003).

Consumption of high-purity gallium in Japan in 2002 was estimated to be 108 tonnes, including domestic production of 8 tonnes, imports of 55 tonnes and scrap recycling of 45 tonnes (Kramer, 2003).

The technology of gallium arsenide processing has been reviewed in detail (Harrison, 1986; Kitsunai & Yuki, 1994). Gallium arsenide can be obtained by direct combination of the elements at high temperature and pressure; it can also be prepared, mainly as a thin film, by numerous exchange reactions in the vapour phase (Sabot & Lauvray, 1994).

Gallium arsenide single crystals are more difficult to fabricate than those of silicon. With silicon, only one component needs to be controlled, whereas with gallium arsenide, a 1:1 ratio of gallium atoms to arsenic atoms must be maintained. At the same time, arsenic volatilizes at the temperatures needed to grow crystals. To prevent loss of arsenic, which would result in the formation of an undesirable gallium-rich crystal, gallium arsenide single-crystal ingots are grown in an enclosed environment. Two basic methods are used to fabricate gallium arsenide ingots: the boat-growth, horizontal Bridgeman or gradient-freeze technique and the liquid-encapsulated Czochralski technique. Ingots produced by the horizontal Bridgeman method are D-shaped and have a typical cross-sectional area of about 2 in^2 [13 cm^2]. In contrast, single-crystal ingots grown by the liquid-encapsulated Czochralski method are round and are generally 3 in [7.5 cm] in diameter, with a cross-sectional area of about 7 in^2 [45 cm^2] (Kramer, 1988; Kitsunai & Yuki, 1994). Ingots grown by the horizontal Bridgeman method are cleaned in chemical baths of aqua regia and isopropyl alcohol, and sandblasted using an abrasive material such as silicon carbide or calcined alumina.

The crystalline orientation of the gallium arsenide ingot is checked by X-ray diffraction and the ends are cut off with a diamond blade saw. The ingots are shaped by grinding the edges and then sliced into wafers along the proper crystalline axis. Wafers pass through several stages of surface preparation, polishing and testing before they are ready for device manufacture or epitaxial growth. [Epitaxy is a method for growing single crystals in which chemical reactions produce thin layers of materials whose lattice structures are identical to that of the substrate on which they are deposited.] Pure gallium arsenide is semi-insulating and, in order to conduct electricity, a small number of atoms of another element must be incorporated into the crystal structure; this is called doping. Doping is accomplished by either ion implantation or epitaxial growth (Harrison, 1986; Kramer, 1988).

Because of the low yield in processing gallium arsenide for optoelectronic devices or integrated circuits, substantial quantities of scrap are generated during the various processing stages. This scrap has varying gallium (from < 1 to 99.99%) and impurity contents, depending on the processing step from which it results. In processing gallium arsenide scrap, the material is crushed, if necessary, and then dissolved in a hot acidic solution. This acidic solution is neutralized with a caustic solution to precipitate the gallium as gallium hydroxide, which is filtered from the solution and washed. The gallium hydroxide filter cake is redissolved in a caustic solution and electrolysed to recover 3N to 4N gallium metal. This metal may be refined to 6N or 7N gallium by conventional purification techniques (Kramer, 1988).

Available information indicates that gallium arsenide is produced by three companies in Taiwan, China, two companies in Japan, and one company each in China, the Ukraine and the USA (Chemical Information Services, 2003).

1.2.2 *Use*

Gallium arsenide has light-emitting properties, high electron mobility, electromagnetic properties and photovoltaic properties. As a semiconductor, it has several unique material properties which can be utilized in high speed semi-conductor devices, high power microwave and millimetre-wave devices, and optoelectronic devices including fibreoptic sources and detectors. Its advantages as a material for high speed devices are high electron mobility and saturation velocity, and relatively easy growth of semi-insulating substrates which render low parasitics and good device isolation. Other useful properties are controllable band gap by alloying, desirable ionization and optical absorption properties. Gallium arsenide has certain advantages over other semiconductor materials: (1) faster operation with lower power consumption, (2) better resistance to radiation and, most importantly, (3) it may be used to convert electrical into optical signals (Chakrabarti, 1992; Greber, 2003).

In 2002, more than 95% of gallium consumed in the USA was in the form of gallium arsenide for optoelectronic devices and integrated circuits. Analogue ICs were the largest single application for gallium, representing 65% of gallium demand (Kramer, 2003). ICs are used in defence applications, high-performance computers and telecommunications. The developments in gallium arsenide IC technology have been reviewed (Welch *et al.*, 1985; Chakrabarti, 1992). About 34% of the gallium consumed was used in optoelectronic devices, which include LEDs, laser diodes, photodetectors and solar cells. Optoelectronic devices are used in applications such as aerospace, consumer goods, industrial components, medical equipment and telecommunications. The remaining 1% was used in research and development, specialty alloys and other applications (Kramer, 2003).

Many manufacturers have introduced new LEDs based on gallium arsenide technology which offer improvements over current LEDs. In many cases, the new LEDs are brighter, last longer and/or can be used in new applications (Kramer, 2002).

Gallium arsenide wafer manufacturers and some electrical companies produce gallium arsenide epitaxial-growth wafers and LED drips. Vapour-phase epitaxy or liquid-phase epitaxy is used to grow gallium arsenide layers for most LEDs. The super-bright red LEDs are manufactured using liquid-phase epitaxy to grow aluminum–gallium–arsenide on gallium arsenide substrates. Epitaxial growth based on metal–organic chemical vapour deposition (MOCVD) technology is used in manufacturing some types of infrared LEDs used in optocouplers. MOCVD is also used to grow a gallium arsenide layer (buffer layer) on gallium arsenide substrates for low-cost optic fibres dedicated to local area computer networks. Gallium arsenide-based laser diodes are manufactured using liquid-phase epitaxy, MOCVD and molecular beam epitaxy technologies (Kitsunai & Yuki, 1994; Sabot & Lauvray, 1994).

For analogue ICs, the requirements for epitaxy grow at the same rate as frequencies increase. An epitaxial gallium arsenide layer is also required for most microwave devices with frequencies over 20 GHz. Photovoltaic applications require gallium arsenide wafers and epitaxial layers. Night-vision system devices use an epitaxial layer of gallium arsenide applied to one end of a photomultiplier to enhance infrared images. Gallium arsenide epitaxial-growth wafers are is also used in optical ICs and magnetoelectric transducers (Sabot & Lauvray, 1994).

1.3 Occurrence and exposure

1.3.1 *Natural occurrence*

Gallium arsenide does not occur naturally. Gallium is present in the earth’s crust at 5–15 mg/kg and is recovered as a by-product of the extraction of aluminum and zinc from their ores (Beliles, 1994; Sabot & Lauvray, 1994).

Arsenic concentration in the earth’s crust is generally < 2 mg/kg, but may be elevated in zones of active or extinct volcanic activity (IARC, 2004).

1.3.2 *Occupational exposure*

Exposure to gallium arsenide occurs predominantly in the microelectronics industry where workers are involved in the production of gallium arsenide crystals, ingots and wafers, in grinding and sawing operations, in device fabrication, and in sandblasting and clean-up activities (Webb *et al.*, 1984; Harrison, 1986). The National Institute for Occupational Safety and Health (NIOSH) estimated that in 1981 the microelectronics industry employed approximately 180 000 workers in the USA, with over 500 plants manufacturing semiconductors (National Institute for Occupational Safety and Health, 1985).

Exposure to gallium arsenide can only be monitored by determining arsenic concentrations. Several reports describe the assessment of exposure to arsenic during gallium arsenide production and use (Harrison, 1986; Yamauchi *et al.*, 1989; Sheehy & Jones, 1993). Harrison (1986) reported short-term exposure concentrations of arsenic measured at two facilities during epitaxial vacuum servicing and beadblasting of 0.29 and 2.5 mg/m^3, respectively.

Sheehy and Jones (1993) conducted more thorough workplace assessments of total arsenic exposure during 1986–87 by collecting personal breathing zone and workplace air samples at various stages of gallium arsenide production in three different plants. In areas where arsine gas was used, arsine concentrations were also measured. In general, arsenic concentrations in air in personal breathing zones were found to be < 5 μg/m^3 in each of the three plants. However, concentrations in air samples collected from personal breathing zones of individuals responsible for cleaning activities in the crystal-growth area were as high as 2.7 mg/m^3. Wipe samples collected from various work sites showed mean concentrations up to 970 μg/100 cm^2. The authors noted that in two of the three plants monitored, 30–70% of the arsenic collected in air in personal breathing zones passed through the filters and was collected on charcoal tubes, implying that a large portion of the exposure to arsenic was due to arsine gas. The authors concluded that in order to determine exposure to arsenic during gallium arsenide production, both particulate and gaseous arsenic should be monitored.

Yamauchi *et al.* (1989) measured inorganic arsenic, MMA^V, DMA^V and trimethylarsenic compounds in the urine and hair of workers involved in various stages of gallium arsenide crystal and wafer production. Total arsenic concentration in workplace air ranged from 2 to 24 μg/m^3. For workers in these areas, the mean concentration of total arsenic in hair was significantly greater than that in the controls and ranged from 1.11 to 6.28 μg arsenic per g of hair, with inorganic arsenic contributing 85–99.6% of total arsenic. [The Working Group noted discrepancies between the means and ranges of concentrations of arsenic species in hair, and between text and table in the percentage of inorganic arsenic over total arsenic.] There was no difference in DMA^V concentrations in hair between workers and controls (approximately 0.03 μg/g arsenic), and MMA^V and trimethylarsenic compounds were not detected in either group. Of the arsenic species detected in urine, trimethylarsenic compounds were the most abundant, followed by DMA^V, inorganic arsenic and MMA^V. There was no difference between pre- and postwork concentrations for any of the arsenic species analysed. The authors suggested that the high concentrations observed were possibly due to the high consumption of seafood containing arsenic (arsenobetaine and arsenocholine) by workers in Japan. They concluded that urinary arsenic could be used as a biomarker of exposure only if speciation analyses are performed (see also Section 1.1.5(*b*)(ii)); determination of arsenic in hair, on the other hand, was suggested for environmental monitoring of arsenic.

A study was conducted to examine the relationship between total arsenic concentrations in hair of employees in a semiconductor fabrication facility and their job responsibility (de Peyster & Silvers, 1995). Airborne arsenic was found in areas where equipment was cleaned but not in administrative areas. The highest arsenic concentration found in the study (15 μg/m^3) was in an air sample collected over a period of 2 h in the breathing zone of an employee cleaning a source housing in an area with local exhaust ventilation. A concentration of 2 μg/m^3 was found during the remainder of the cleaning period (~53 min). Maintenance workers who were regularly assigned to cleaning equipment, and therefore presumed to have the highest potential exposure, had a mean concentration of arsenic in hair of 0.042 μg/g. This was slightly higher than the mean of 0.033 μg/g observed in controls working in administrative areas, but the difference was not statistically significant. Maintenance workers who only occasionally cleaned and maintained arsenic-contaminated equipment had a mean arsenic concentration in hair of 0.034 μg/g. The highest mean concentration of arsenic in hair, 0.044 μg/g, was found in the group of supervisors and engineers. However, the highest concentrations in this group (0.076 and 0.106 μg/g) were observed in two heavy smokers. When smokers were eliminated from the analysis, means increased according to levels of presumed occupational exposure. Sex, tap-water consumption and dietary habits may also have affected arsenic concentrations in hair.

1.4 Regulations and guidelines

The only occupational exposure limit for gallium arsenide in the available literature was reported by NIOSH. NIOSH recommended a ceiling value of 0.002 mg/m^3 for gallium arsenide (ACGIH Worldwide®, 2003). No occupational exposure limits have been set for gallium.

Occupational exposure limits and guidelines for arsenic in some countries are presented in Table 1. Regulations and guidelines for arsenic in drinking-water were summarized recently by IARC (IARC, 2004).