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REVIEW

Industries using arsenic and arsenic compounds

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This paper reviews industries using arsenic and arsenic compounds such as wood preservatives and agricultural chemicals, the use of arsenic trioxide in glass manufacture, and the applications of metallic arsenic in non-ferrous alloys and of high-purity arsenic in the electronics industry.

Keywords: Wood preservatives, agricultural chemicals, high-purity metallic arsenic, gallium arsenide, chalcogenide glass

INTRODUCTION

The raw material of arsenic is arsenic trioxide, which is used at the level of 50 000–53 000 tons per year worldwide.[1,2] The main uses of arsenical products are in wood preservatives and agricultural chemicals in cotton production (desiccants, herbicides). Arsenic trioxide is used in the glass industry as a fining agent to remove tiny dispersed air bubbles and as a decolorizing agent. In the USA restriction of arsenic by the Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA) has extended step by step,[3] and synthesis of arsenic compound for agricultural chemicals and of arsenic trioxide for glass manufacturing has been decreased. Although use of metallic arsenic for copper- and lead-base alloys is tending to decrease also, production of high-purity metallic arsenic[4] for gallium arsenide semiconductors has been increasing gradually.

Arsenic is less toxic in the pentavalent than in the trivalent state, and further, generally speaking, organic arsenical compounds have rather less toxicity than inorganic compounds. For agricultural chemicals the main materials have been changed to organic arsenic compounds from inorganic arsenic compounds. In electronics use,[5] Metal Organic Chemical Vapor Deposition (MOCVD) processes require use of arsine (AsH_3) gas. As this gas is very toxic, organic arsines (toxicity about one-tenth of AsH_3) will gradually become used instead of arsine gas.

A small amount of arsenic is used in animal feed additives, such as arsanilic acid and[6] 3-nitro-4-hydroxyphenylarsonic acid.

This paper reviews arsenic and arsenic industries throughout the world.

2 DEMAND AND SUPPLY OF ARSENIC AND ARSENIC COMPOUNDS

Arsenic trioxide is recovered as a by-product from copper or lead smelting. The most common separation methods are volatilization from ores containing arsenic.[1] Sublimation of arsenic trioxide occurs during the roasting stage of these ores. World production of arsenic trioxide is about 50 000–53 000 tons per year. Table 1 shows world production by country.[2] The USA's sole arsenic trioxide producer, ASARCO (American Smelting and Refining Co.), had terminated copper smelting operations and associated recovery of by-product arsenic trioxide at Tacoma, Washington, in 1985. Therefore imports into the USA for consumption of arsenic trioxide increased significantly, owing to increased demand for arsenical wood preservatives.

The USA consumes about 50% or more of arsenic trioxide production in the world. Table 2 shows arsenic supply–demand relationships in the USA. As domestic production of arsenic trioxide in the USA has been nearly zero, arsenic metal and arsenic compounds consumed in the USA have been imported from France, Chile, Mexico, Sweden, etc. Table 3 shows US imports for consumption of arsenicals, by class and country.

Arsenic compounds, principally arsenic trioxide, account for 98% of arsenic consumed in 1989 in the USA. Demand for arsenic was at about the same level in 1988 as it was in the previous year. Estimated end-use distribution[2] of arsenic in the USA was 70% (16 600 tons as elemental arsenic) in industrial chemicals (principally wood preservatives), 22% (5200 tons) in agricultural chemicals (principally herbicides and desiccants), 4%

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Table 1 World production of arsenic trioxide by country (metric tons)[a]

Country[b]	1985	1986	1987	1988[c]	1989[c]
Belgium[d]	3000	3000	3500	3500	3500
Bolivia	361	241	132	191	350
Canada[d]	3000	3000	2000	2000	2000
Chile	4000	4000	3616	3207	3400
France[d]	8000	10 000	10 000	10 000	10 000
FRG[d]	360	360	360	360	360
Japan[d]	500	500	500	500	500
Mexico	4782	2208	2983	5164	5100
Namibia	2471	2208	1864	2983	2900
Peru	1257	1273	1757	828	1000
Philippines[d]	5000	5000	5000	5000	5000
Portugal	204	176	218	214	180
Sweden[d]	10 000	10 000	10 000	10 000	10 000
USSR[d]	8100	8100	8100	8100	8100
USA	2200	—	—	—	—
Total	53 235[e]	53 173[e]	52 351	52 047	53 390

[a] from Ref. 2. Including calculated arsenic trioxide equivalent of output of arsenic compounds other than arsenic trioxide where inclusion of such materials would not duplicate reported arsenic trioxide production. The table includes data available by 25 May 1990.

[b] Austria, China, Czechslovakia, the German Democratic Republic, Hungary, the Republic of Korea, Spain, the UK and Yugoslavia, have produced arsenic and/or arsenic compounds in previous years, but information is inadequate to make reliable estimates of output levels, if any.

[c] Preliminary figures. [d] Estimated. [e] Revised.

(900 tons) in glass manufacture, 3% (700 tons) as metallic arsenic in non-ferrous alloys, and 1% (300 tons) for other uses (animal feed additives, pharmaceuticals, etc.) in 1989.

Before 1970 the most common of the wood preservatives was creosote oil,[3] but after 1970 arsenical wood preservatives increased gradually. Therefore use of creosote oil for wood preservatives has decreased to 10–15% of all wood preservatives now. Arsenical wood preservatives[7] is produced in Europe (including Finland, Sweden, Norway, Denmark), New Zealand and also Japan.

The major use of arsenical chemicals in agriculture is in cotton production, where they are used as herbicides and plant desiccants and defoliants. The arsenical herbicides monosodium methylarsonate (MSMA) and disodium methylarsonate (DSMA) are produced from arsenic trioxide.

Zinc producers used arsenic trioxide as a collector to separate zinc from copper, cobalt and nickel. Arsenic and other elements were collected in a residue called copper cake and were sent to the copper producer. Arsenic trioxide for zinc production and glass manufacture is consumed at the level of 220–230 tons per year in Japan. These are two major uses, but arsenic trioxide for wood preservative consumes only 100 tons per year in Japan.

A relatively small amount of high-purity arse-

Table 2 Arsenic supply–demand relationships in US

	Arsenic content (metric tons)					
	1984	1985	1986	1987	1988	1989
US supply:						
Refinery production	5200	1700	—	—	—	—
Imports, metal	300	400	400	600	600	900
Imports, compounds	12 000	13 600	20 200	21 100	21 700	22 800
Industry stocks, 1 Jan.	3100	3300	900	400	200	100
Total	20 600	19 000	21 500	22 100	22 500	23 800
Distribution of US supply:						
Industry stocks, 31 Dec	3300	900	400	200	100	100
Apparent demand	17 300	18 100	21 100	21 900	22 400	23 700
Estimated US demand pattern:						
Agricultural chemicals	5500	4500	5300	5000	5200	5200
Glass	1000	700	800	900	900	900
Industrial chemicals	9900	12 100	14 100	15 100	15 500	16 600
Non-ferrous alloys and electronics	500	400	400	400	400	700
Other	400	400	500	500	400	300
Total	17 300	18 100	21 100	21 900	22 400	23 700

Table 3 US imports for consumption of arsenicals, by class and country
Source: Bureau of the Census, USA

	1987		1988		1989	
Class and country	Quantity (metric tons)	Value ($\$\times 10^3$)	Quantity (metric tons)	Value ($\$\times 10^3$)	Quantity (metric tons)	Value ($\$\times 10^3$)
Arsenic trioxide:						
Belgium	1643	1325	1563	1241	1425	881
Bolivia	16	10	—	—	—	—
Canada	2012	703	2068	1589	1771	799
Chile	4800	1935	6709	2648	5057	1926
China	233	136	18	8	—	—
Finland	—	—	—	—	414	191
France	5341	3180	6909	3664	7059	2977
FRG	—	—	16	13	17	28
Hong Kong	36	18	54	42	18	9
Iran	241	87	—	—	—	—
Japan	48	33	1	3	—	—
Korea	102	70	—	—	—	—
Mexico	4457	3550	4187	3064	4008	2361
Namibia	93	60	—	—	—	—
Philippines	1280	436	1850	792	2727	979
Republic of South Africa	1380	848	1017	559	94	53
Sweden	4824	4140	3664	2836	5676	3262
Switzerland	307	248	—	—	77	50
UK	30	22	—[a]	2	5	10
Total[b]	26 843	16 800	28 056	16 461	28 348	13 526
Arsenic acid:						
Australia	16	28	—	—	—	—
British Virgin Islands	—	—	7	9	—	—
Canada	—	—	—	—	15	17
Netherlands	—	—	—[a]	1	—	—
UK	1038	824	181	161	33	50
Total	1054	852	188	171	48	67
Arsenic sulfide:						
Canada	—	—	12	2	—	—
FRG	15	10	15	29	—	—
Taiwan	—	—	—	—	2	19
Total	15	10	27	31	2	19
Arsenic metal:						
Belgium	2	18	—	—	—	—
Canada	16	1054	19	899	85	658
China	463	972	421	675	627	649
Dominican Republic	—[a]	1	—	—	—	—
France	—	—	—	—	1	1
FRG	2	174	1	162	3	136
Hong Kong	139	291	75	139	124	129
Japan	9	951	5	613	74	508
Mexico	—	—	78	137	—	—
Sweden	—[a]	1	—	—	—	—
UK	—[a]	8	—[a]	17	14	69
Total	631	3471	600	2642	928	2150

[a] Less than $\frac{1}{2}$ metric ton.

[b] Data may not add to totals shown because of independent rounding.

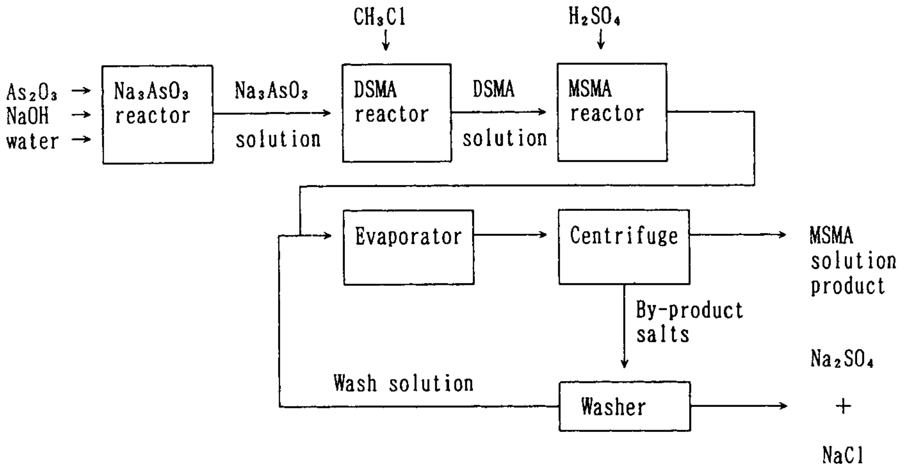


Figure 1 Production scheme for monosodium methanearsonate (MSMA).

nic metal is used in the electronics industry. Gallium arsenide and its alloys are used in such products as light-emitting diodes, semiconductor lasers, discrete microwave devices, solar batteries, Hall devices, and so on.

High-purity arsenic is consumed at a level of 150–200 tons per year world wide. As this is at present only 0.3–0.4% of all arsenic oxide, production of gallium arsenide will probably grow to become the most valuable arsenic industry in the near-future.

3 INDUSTRIES USING ARSENIC AND ARSENIC COMPOUNDS

3.1 Industrial chemicals (principally wood preservatives)

Arsenical wood preservatives for pressure-treating lumber were the largest end-use of arsenic trioxide. There are three types of arsenic wood preservatives,[3,7] viz. chromated copper arsenate (CCA), ammoniacal copper arsenate (ACA) and fluorchrome arsenate phenol (FCAP). CCA is the most used arsenical wood preservative; ACA and FCAP are less widely used.[3]

In the preparation of chromated copper arsenate (CCA), arsenic acid (H_3AsO_4) is mixed with copper oxide (CuO) and chromic oxide (Cr_2O_3) to form a leach-resistant waterborne preservative for pressure-treating lumber. CCA reacts chemically with the wood substrate, or is fixed to form a highly leach-resistance and durable product. Arsenical wood preservatives are used to prevent rot or insect damage to wood, in such applications as construction lumber, timber, fenceposts and utility poles, and in marine uses.

The major market for arsenic is for its use in wood preservatives. The future for arsenic consumption is therefore tied to new housing developments, where wood decks containing arsenical preservatives have become almost standard items in recent years in some countries. People adding decks to existing houses also use treated wood. Over the next five years, the growth of wood preservatives is expected to average 3–5% per year, much less than in previous years. No major environmental problems associated with the use

Table 4 Properties of methanearsonic acid [$CH_3AsO(OH)_2$]

	Acid	Monosodium salt	Disodium salt
Melting point (°C)	154.4–5.5 (Loses water at 130)	Dehydrates	Decomposes (Hexahydrate, 132–139)
Solubility in water (g/100 g)	28	75	39.6
pH of water solution	2.6	6.4	10.2

of arsenicals in wood preservatives are anticipated because of the small amounts of arsenic involved, and the fact that arsenic does not leach from treated wood.[2]

3.2 Agricultural chemicals (herbicides and desiccants)

The major use of arsenic chemicals[8] in agriculture is in cotton production, where arsenic acid is used as a desiccant in a mechanical stripper harvesting of cotton. Arsenic acid production has decreased significantly from earlier years when lead arsenate and calcium arsenate were used extensively as insecticides. Arsenic acid is prepared by oxidation of arsenic trioxide with nitric acid. These latter are mixed in a stoichiometric ratio and heated to 80–100 °C to cause the reaction to proceed. All of the by-products volatilize and the final product composition is controlled by the extent of heating. Several distinct hydrates are known by thermogravimetric and differential thermal analyses. These are $As_2O_5.4H_2O$, $As_2O_5.3H_2O$, $2As_2O_5.5H_2O$, $As_2O_5.2H_2O$, and $2As_2O_5.5H_2O$. The herbicidal form is $As_2O_5.2H_2O$. Copper–chromium arsenate is prepared by mixing the stoichiometric amount of arsenic acid with copper and chromium oxides.

Methanearsonic acid $[CH_3A_3O(OH)_2]$ is prepared and marketed alost exclusively as its mono- and di-sodium salts. These are effective contact herbicides for a number of broadleaf and grassy weeds, particularly in cotton and citrus growing.

Table 5 Properties of cacodylic acid $[(CH_3)_2A_3O(OH)]$

	Acid	Sodium salt
Melting point (°C)	192.0–192.5	>330
Solubility in water (g/100 g)	217 (25 °C) 355 (72 °C)	51 (25 °C)
Solubility in ethanol (g/100 g)	19.5 (15 °C) 82.0 (b.p.)	
pH of water solution	4.2	8.2

The production follows essentially the following steps (Eqns [1]–[3]).[8,9]

$$As_2O_3 + 6NaOh \rightarrow 2Na_3AsO_3 + 3H_2O \qquad [1]$$

$$Na_3AsO_3 + CH_3Cl \rightarrow Na_2As(CH_3)O_3 + NaCl \quad \text{DSMA} \qquad [2]$$

$$2Na_2As(CH_3)O_3 + H_2SO_4 \rightarrow 2NaHAs(CH_3)O_3 + Na_2SO_4 \quad \text{MSMA} \qquad [3]$$

A schematic of the process is presented in Fig. 1.

The first step involves mixing arsenic trioxide with caustic soda. This reaction is exothermic, and the hot solution is transferred to the DSMA reactor where methyl chloride is pressured in and the reaction proceeds at about 60 °C with agitation. The solution is then transferred to another tank where sufficient sulfuric acid is added to form MSMA. This tank is lined with or composed of a material resistant to acid in order to avoid

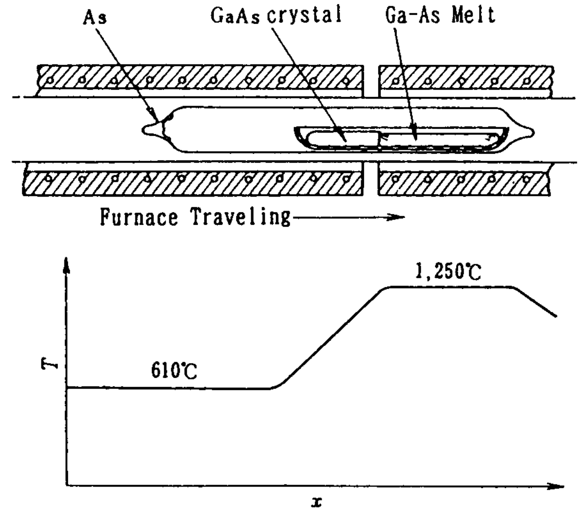


Figure 2 Horizontal Bridgeman method.

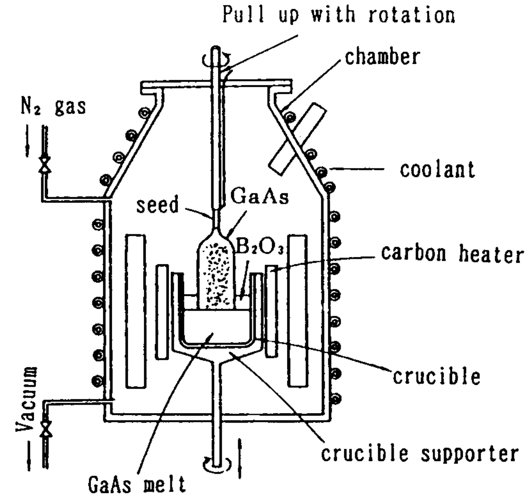


Figure 3 Liquid encapsulated Czochralski method.

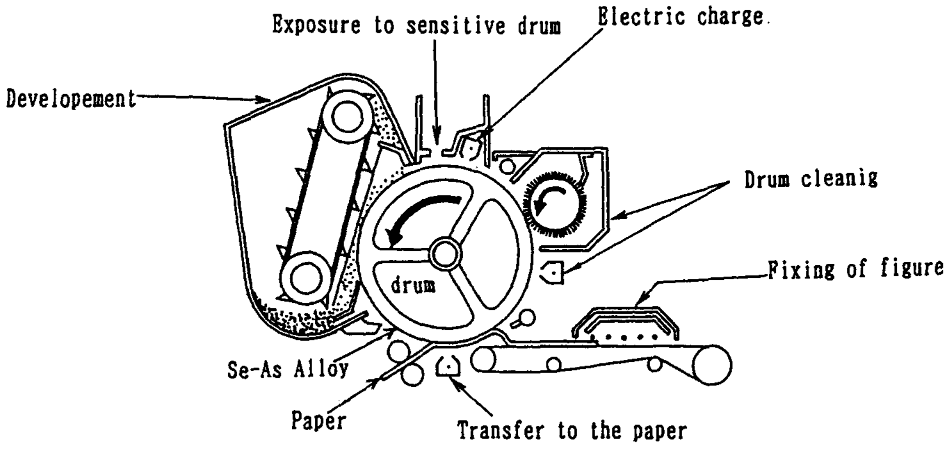


Figure 4 Sketch of copy machine.

corrosion in case of a processing error. The mixture of MSMA, sodium chloride and sodium sulfate is separated by a combination of evaporation and centrifugation. The salts are washed to recover entrained MSMA.

Some of the physical properties of methanearsonic acid and its sodium salts are given in Table 4.

Cacodylic acid [$(CH_3)_2AsO(OH)$] is also a herbicide made from arsenic trioxide (Table 5). It is used as a cotton defoliant and as a non-selective contact herbicide on non-crop areas.

When starting with disodium methaneasonate (DSMA), production follows Eqns [4]–[7].[8,10]

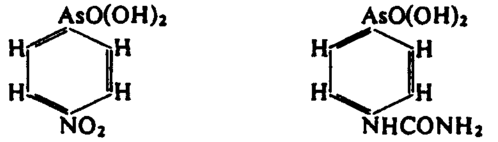
$$Na_2As(CH_3)O_3 + H_2SO_4 \rightarrow H_2As(CH_3)O_3 + Na_2SO_4 \qquad [4]$$

Table 6 Uses of gallium arsenide devices

GaAs device	Epitaxial layer/ GaAs wafer	Uses
Light-emitting diodes (LED)		
Visible LED	GaAlAs/GaAs GaAsP/GaAs	Indicators, figure indicators, high stop lamps, LED printers
Infrared LED	GaAs/GaAs	Photocouplers, photo-interruptors
	GaAlAs/GaAs	Communications, automatic cameras
Laser diodes (LD)		
Visible LED	GaAlAs/GaAs	Laser printers, communications
Infrared LED	GaAs/GaAs	Communications
	GaAlAs/GaAs	Compact disks, laser disks
Microwave devices	GaAs/GaAs	Laser printers, communications
Field-effect transistors (FET)	GaAs/GaAs	Personal telephones, microwave monolithic integral circuits (MMIC)
High electron mobility transistors (HEMT)	GaAlAs/GaAs	Satellite broadcast receivers, personal telephones
GaAs integrated circuits	GaAs/GaAs	High-speed computers
Opto-electronic integral circuits (OEIC)	GaAlAs/GaAs	High-speed computers (in the future)
Hall devices	Ion implantation with GaAs wafer	No explosion motors, magnetic sensors
Photo detectors	GaAlAs/GaAs	Communications, detectors
Solar batteries	GaAs/GaAs	Electric power for satellites

Arsanilic acid (poultry and swine)

3-Nitro-4-hydroxyphenylarsonic acid (poultry and swine)



4-Nitrophenylarsonic acid (turkeys)

***p*-Ureidobenzenearsonic acid (turkeys)**

Figure 5 Animal feed additives.

$$H_2As(CH_3)O_3 + SO_2 \rightarrow CH_3AsO + H_2SO_4 \qquad [5]$$

$$CH_3AsO + 2NaOH \rightarrow Na_2As(CH_3)O_2 + H_2O \qquad [6]$$

$$Na_2As(CH_3)O_2 + CH_3Cl \rightarrow NaAs(CH_3)_2O_2 \qquad [7]$$

$$+ NaCl \quad \text{Sodium cacodylate}$$

DSMA is neutralized, sulfur dioxide is added with sufficient agitation, and the mixture is transferred to a tank containing sufficient caustic soda to neutralize both the arsenomethane and the sulfuric acid formed during the reduction. Methylation proceeds within a few hours at about 60 °C. The mixture is evaporated and centrifuged to remove the salts from the desired product.

The use of arsenic in agricultural chemicals has been under close scrutiny by the US Environmental Protection Agency (EPA) for many years. Many pesticide uses for arsenical chemicals have been banned by the EPA. The use of the arsenicals DSMA, MSMA, arsenic acid and cacodylic acid on cotton is expected to remain stable or to decline over the next five years.[2]

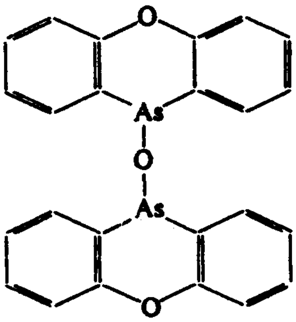


Figure 6 Chemical structure of 10,10'-oxybisphenoxarsine.

3.3 Glass manufacture

Arsenic trioxide is used in the glass industry as a fining agent to remove tiny dispersed air bubbles, and as a decolorizing agent. At high temperatures, As_2O_3 reduces Fe_2O_3 to FeO, while As_2O_3 itself is oxidized to As_2O_5 (Eqn. [8]).

$$As_2O_3 + 2Fe_2O_3 \xrightarrow{800\text{–}1\,000\,°C} As_2O_5 + 4FeO \qquad [8]$$

Recently, however, glass manufacturing companies have eliminated or reduced to minimum amounts their consumption of arsenic compounds. Selenium and cerium are alternatives in glass.[11]

3.4 Metallic arsenic in non-ferrous alloys

The bulk of metallic arsenic is used in lead- and copper-based alloys as a minor additive (0.01–0.5%) to increase strength in posts and grids of lead acid-storage batteries and to improve corrosion resistance and tensile strength in copper alloys.

Calcium–lead alloys may substitute for antimony–lead–arsenic alloys in car storage batteries.[11]

3.5 High-purity metallic arsenic for the electronics industry

Semiconductor devices require extreme high purity in their source materials. The most important process to obtain high-purity arsenic is indicated in the following reaction sequences (Eqns [9], [10]).

$$As_2O_3 + 6HCl \rightarrow 2AsCl_3 + 3H_2O \qquad [9]$$

$$4AsCl_3 + 6H_2 \rightarrow As_4 + 12HCl \qquad [10]$$

One of the most important factors of this process is to start with 99% pure As_2O_3 and carefully to purify the intermediate $AsCl_3$ before reduction. Some purification, primarily the removal of sulfur and selenium, still occurs during the reduction step, but most must be accomplished before this age. Arsenic trichloride is manufactured by the reaction of arsenic trioxide with hydrogen chloride in a packed tube. A packed tube can be used essentially for a continuous process. The vapors are condensed in a separation tank, where two phases form. The upper layer is aqueous hydrogen chloride (hydrochloric acid) containing about 17.5% $AsCl_3$ and the bottom layer is 99% $AsCl_3$.[4]

High-purity $AsCl_3$ is obtained by fractional distillation.

Reduction of arsenic trichloride with hydrogen to elemental arsenic is carried out by passing a mixture containing two to four times the necessary amount of hydrogen through a tubular reactor. The temperature is maintained at 800–900 °C.[12] The best equation (Eqn [11]) to describe the reaction for the reduction is:

$$AsCl_3 + 1.5H_2 = 0.25As_4 + 3HCl \qquad [11]$$

High-purity metallic arsenic is used for gallium arsenide and arsenic selenide (chalcogenide glass).

Gallium arsenide-based devices are developed and manufactured for communications and computing; the requirements for high-quality gallium arsenide materials are becoming more stringent.

The materials requirements can be divided into device types. Optoelectronics devices such as lasers, light-emitting diodes and solar cells typically require material with a low density of dislocations. High-speed devices, including microwave field-effect transistors (FET) and integrated circuits (IC), require material with a low impurity level.

Two gallium arsenide crystal-growth technologies predominate. The horizontal Bridgeman (HB) technique employs a horizontal crucible (or boat) to contain the melt and the seed crystal. The boat is surrounded by an evacuated quartz enclosure (or ampoule) and the entire assembly is positioned in a multizone, high-temperature furnace (Fig. 2). The growth process takes place by moving a temperature gradient across the melt, thereby freezing the molten gallium arsenide from the seed down the length of the crystal.

The advantage of this process is that the temperature gradients are low and well-controlled. The liquid-encapsulated Czochralski (LEC) process uses a modification of the Czochralski processes, which is used for silicon-crystal growth. In this technique, a crucible is encapsulated in a layer of boric oxide. This oxide prevents arsenic vapor from escaping from the melt and coating the cold walls of the growth chamber (Fig. 3). A seed crystal is attached to pull rod, which is lowered as the melt temperature is reduced to just above the melting point, and then the crystal growth of the gallium arsenide seed begins. The seed crystal pull rate and the temperature of the melt are regulated to control the growth process.

An advantage of this technique is that the crystal is grown without a crucible and occurs in a cylindrical shape. This allows the production of round wafers, which are sliced parallel to the interface. Also, since the melt is encapsulated by relatively non-reactive boric oxide, the background-impurity levels are very low.

Gallium arsenide has several advantages[5] over silicon semiconductors, such as light-emitting properties, high electron mobility, high-temperature durability, radiation durability and responsiveness to magnetic fields.

In the preparation of gallium arsenide (GaAs) devices, epitaxial growth on the GaAs surface is most important. There are two ways of providing epitaxial growth processes in GaAs: metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). Harrison and Tompkins[13] produced a high-resistivity film believed to be GaAs by heating equimolar amounts of trimethylgallium and arsine to 200 °C.

The first report of the organometallic-hydride CVD process for producing single-crystal semiconductor films was an open-tube process which was performed by Manasevit[14] in 1968 and subsequently described[15] in 1969. Hydrogen as a carrier gas was bubbled through either triethylgallium or trimethylgallium and the vapors of the alkylgallium were mixed with arsine and pyrolyzed at 650–750 °C to produce single-crystal films of GaAs on both single-crystal semiconductors and insulators. In simplified form the reaction may be expressed (Eqn [12]) as:

$$(CH_3)_3Ga + AsH_3 \xrightarrow{H_2} GaAs + 3CH_4 \qquad [12]$$

Replacing arsine by other Group V hydrides such as phosphine (PH_3) produced gallium phosphide (GaP) while pyrolysis of hydride mixtures such as arsine and phosphine or arsine and stibine, with trimethylgallium vapor led to single-crystal films of $GaAs_{1-x}P_x$, and $GaAs_{1-x}Sb_x$, respectively. Replacing stibine with trimethylantimony also produced $GaAs_{1-x}Sb_x$.

Manasevit and co-workers[16] extended the organometallic CVD process to produce other semiconductor compounds. Aluminium arsenide (AlAs) was prepared by pyrolyzing mixtures of trimethylaluminum and arsine. Alloys of $Ga_{1-x}Al_xAs$ were relatively easily formed by adding trimethylgallium to trimethylaluminum and arsine mixtures before pyrolysis.

In order to reduce dangerous procedures, trimethylarsine $[(CH_3)_3As]$, triethylarsine $[(C_2H_5)_3As]$, tert-butylarsine$[(CH_3)_3CAsH_2]$ and dimethylarsine $[(C_2H_5)_2AsH]$ are used instead of toxic arsine (AsH_3).

Arsenic-containing selenium glass (chalcogenide glass) is used in the photoconductors of copy machines. If arsenic selenide compounds are used, the copy machine has a ten times higher speed than that using selenium only. Figure 4 shows a sketch of a copy machine. Following this, chalcogenide glass (with an elemental composition near As_2Se_3) is used in laser printers which have the ability to operate at higher speeds.

Various uses of gallium arsenide (GaAs) devices are shown in Table 6.

3.6 Other uses of arsenic

A small amount of arsenic is used for animal feed additives. Four arsenic compounds are now used in animal husbandry. Figure 5 gives the structures of these animal feed additives. Their production is more appropriate to organic chemistry than specifically to arsenic chemistry, but a brief description illustrates their preparation.

Arsanilic acid[6] is produced by adding a solution of arsenic acid and benzene slowly to a mixture of excess aniline in perchloroethylene held at 130 °C. Water is distilled azeotropically from the mixture as it is formed, the excess aniline is stripped, and an acid hydrolysis converts the intermediate bis(*p*-aminophenyl)arsenic acid to arsanilic acid. The product is recrystallized before use.

The heterocycle 10,10′-oxybisphenoxarsine (Fig. 6) is manufactured[17] and marketed as an antimicrobial agent which is particularly useful in conjunction with plastics.

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REFERENCES

1. Minor Metals Yearbook. In: US Bureau of Mines, Washington DC, 1988, *Minerals Yearbook 1988*, pp 1059–1062
2. Loebenstein, J Arsenic. In: *Minerals Yearbook 1989*, US Bureau of Mines, Washington DC, 1989, pp 123–126
3. Edelstein D L, *Mineral Facts and Problems*, US Bureau of Mines, 1985, pp 43–52
4. Ishiguro, S In: *Joint Symposium, Kyoto, 1989*, The Mining and Materials Processing Institute of Japan/The Institute of Mining and Metallurgy of the UK, pp 539–547
5. Oikawa, K *Appl. Organomet. Chem.*, 1988, 2: 391
6. Nemec, J W, Raterink H R and Wise S W US Patent 3 586 708, 1971
7. Baldwin, W J *The Use of Arsenic as a Wood Preservative*, Lederer, W and Fensterheim, R (eds), Van Nostrand Reinhold, New York, 1983, pp 99–107
8. *Encyclopedia of Chemical Processing and Design*, vol 3, Marcel Dekker Inc., New York, Basel, 1977, pp 396–417
9. Miller, G E and Reid, E E US Patent 2 695 306, 1954
10. Moyerman, R M and Ehman, P J, US Patent 3 173 937, 1965
11. *Minerals Handbook 1988–89*, pp 37–42, Phillip Crowson, M. Stockton Press
12. Mueller, L and Hoake, G *Freiberg Forschung* 1963, B83: 5
13. Harrison B and Tompkins E H, *Inorg. Chem.*, 1962, 1: 951
14. Manasevit, H M *Appl. Phys. Lett.*, 1968, 12: 156
15. Manasevit, H M and Simpson, W I *J. Electrochem. Soc.*, 1969, 116: 1725
16. Manasevit, H M *J. Electrochem. Soc.*, 1971, 118: 647
17. Yeager, C C and Ellyn G US Patent 3 288 674, 1966