Information Circular 9208

Gallium and Gallium Arsenide: Supply, Technology, and Uses

By Deborah A. Kramer

UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
T S Ary, Director

Library of Congress Cataloging in Publication Data:

Kramer, Deborah A.
Gallium and gallium arsenide.

(Information circular / United States Department of the Interior, Bureau of Mines; 9208)

Bibliography: p. 25.

Supt. of Docs. no.: I 28.27:9208.

1. Gallium industry. 2. Gallium arsenide industry. I. United States. Bureau of Mines. II. Title.

TN295.U4 [HD9539] 622 s [338.4'76610675] 88-600326

CONTENTS

	Page
Abstract	1
Introduction	2
Uses	2
Optoelectronic devices	2
Integrated circuits	3
Analog ICs	3
Digital ICs	3
Other applications	4
Properties and grades	4
Resources	5
Recovery technology	9
Gallium recovery from bauxite	9
Gallium recovery from zinc ore	10
Gallium recovery from other sources	10
Gallium purification	11
Gallium arsenide fabrication	11
Secondary recovery	15
World supply and demand	16
Production	16
Trade	16
Domestic demand	16
Structure of the industry	18
Gallium recovery, recycle, and purification	18
Australia	18
Canada	18
China	18
Czechoslovakia	18
France	19
Federal Republic of Germany	19
Hungary	20
India	20
Japan	20
Norway	20
Spain	20
Switzerland	20
U.S.S.R.	20
United Kingdom	20
United States	21
High-purity arsenic production	21
Gallium arsenide ingot, wafer, and device manufacturers	21
Research and development	23
Legislation and Government programs	24
Strategic factors	24
References	25

ILLUSTRATIONS

Page

1. Beja process for recovering crude gallium from Bayer liquors 9
2. de la Breteque process for recovering crude gallium from Bayer liquors 10
3. Gallium recovery from zinc ore 10
4. Gallium recovery from Musto Explorations Ltd.'s mine near St. George, UT 11
5. Elkem A/S process for recovering gallium from aluminum smelter flue dust 12
6. GaAs ingot growing in LEC furnace 13
7. LEC-grown GaAs ingot and wafers 13
8. GaAs wafer with devices 14

TABLES

1. Gallium reserves and reserve base 6
2. World alumina plant capacities and gallium potential, yearend 1987 7
3. World primary gallium production 16
4. World secondary gallium production 17
5. U.S. gallium imports for consumption, by country 17
6. Japanese gallium imports, by country 17
7. Gallium supply-demand relationships, 1977-87 18
8. Yearend gallium plant capacities 19
9. Gallium arsenide ingot, wafer, and device manufacturers 21
10. U.S. import duties for gallium, January 1, 1989 24

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mt	metric ton
GHz	gigahertz	nm	nanometer (one billionth of a meter)
in	inch	pct	percent
in^2	square inch	ppba	part per billion atomic
kg	kilogram	ppm	part per million
kg/yr	kilogram per year		

GALLIUM AND GALLIUM ARSENIDE: SUPPLY,TECHNOLOGY, AND USES

By Deborah A. Kramer[1]

ABSTRACT

As part of the Nation's growing concern with the competitiveness of U.S. firms in the world economy, especially with respect to advanced materials, the Bureau of Mines assessed the actual and potential recovery and manufacturing capabilities for gallium and gallium arsenide (GaAs). GaAs has advanced from a laboratory curiosity to a material with important "high-tech" applications within only the last few years, and although protected North American gallium supplies are currently considered adequate, consumption could grow to the point that this assessment would need reevaluation.

[1]Physical scientist, Division of Mineral Commodities, Bureau of Mines, Washington, DC.

INTRODUCTION

Gallium-based components can be found in a variety of products ranging from compact disk players to advanced military electronic warfare systems. Compared with silicon, a material GaAs has replaced in some of these applications, components made of GaAs can emit light, have greater resistance to radiation, and operate at a faster speed and higher temperatures. But GaAs components are more costly and more difficult to fabricate than those of silicon, so they are used only in applications where the advantage of their properties significantly outweighs their cost disadvantage.

Gallium occurs in very low concentrations in the Earth's crust, and virtually all primary gallium is recovered as a byproduct, principally from processing bauxite to alumina. Most of gallium's applications require very high purity levels, and the metal must be refined before use until it contains no more than 1 ppm of total impurities. Most gallium metal recovery and refining facilities are in Europe. Through complex processing techniques, GaAs single crystals are produced, and optoelectronic devices and integrated circuits (ICs) are fabricated. Japan and the United States lead the world in GaAs crystal and device fabrication. Considerable investments are being made to increase processing efficiency, develop new devices, and increase the applications of current GaAs-based components.

USES

Gallium has limited commercial applications in its metallic form. Its principal use is in the manufacture of semiconducting compounds, mainly GaAs and gallium phosphide (GaP). Over 90 pct of the gallium consumed in the United States is used for optoelectronic devices and ICs. Optoelectronic devices–light-emitting diodes (LEDs), laser diodes, photodiodes, and solar (photovoltaic) cells–take advantage of GaAs's ability to convert electrical energy to optical energy and the reverse. The principal market for optoelectronic devices is in nonmilitary applications, including communications systems and consumer electronic goods. GaAs-based integrated circuits are used primarily in defense applications, although developments in recent years have increased their use in the commercial sector. GaAs-based integrated circuits are important, particularly in defense applications, because they can send information about five times faster, can withstand more radiation, and can operate at higher temperatures than comparable silicon-based integrated circuits.

OPTOELECTRONIC DEVICES

An LED is a semiconductor that emits light when an electric current is passed through it. LEDs have been in commercial use for many years. The first commercial applications for LED technology were in displays for hand-held calculators and digital watches. Today, LEDs are used in visual displays in automobiles, calculators, appliances, consumer electronic equipment, and a wide variety of industrial equipment. LEDs are also used as a light source in short-distance fiber optic communications systems.

LEDs consist of layers of an epitaxially grown material on a substrate. These epitaxial layers are normally gallium aluminum arsenide (GaAlAs), gallium arsenide phosphide (GaAsP), or indium gallium arsenide phosphide (InGaAsP); the substrate material is either GaAs or GaP. The materials used to fabricate LEDs determine the color of light that is emitted. With GaP substrates, the wavelength of light can cover the spectrum from 555 nm, pure green, to about 700 nm, red. With GaAs substrates, light emitted from an LED is limited to wavelengths at the red and infrared end of the spectrum.

Laser diodes operate on the same principle as LEDs, but they convert electrical energy to a coherent light output. Laser diodes, also called semiconductor lasers or injection laser diodes, principally consist of an epitaxial layer of GaAs, GaAlAs, or InGaAsP on a GaAs substrate. The two most commonly used laser diodes are GaAlAs and InGaAsP diodes. GaAlAs laser diodes operate at about 780 to 900 nm and are used in a wide variety of consumer products and in communications systems. GaAlAs diodes are used in compact disk players, nonimpact laser printers, and optical video disk players. They are also used in short-range fiber optic communications systems, satellite communications, radar transmission, and local cable transmission systems. InGaAsP laser diodes operate at longer wavelengths, 1,300 to 1,500 nm, and are primarily used for transmission of high-frequency, long-distance signals in fiber optic communication systems and in cable television supertrunks.

Photodiodes, or detectors, are used to detect a light impulse generated by a source, such as an LED or laser diode, and convert it to an electrical impulse. Photodiodes are fabricated from the same materials as LEDs and are used primarily as light detectors in fiber optics systems. There are two types of gallium-based photodiodes–GaAlAs epitaxially grown on a GaAs substrate, used to detect light at short wavelengths, and InGaAsP on an indium phosphide (InP) substrate, used to detect light at longer wavelengths.

Because of its ability to convert light to electrical energy, GaAs is an excellent material for solar cells. Although solar cells are not in widespread use, they have been used to power communications satellites. GaAs's advantage in this application is its electrical conversion efficiency; GaAs solar cells have been demonstrated to

convert 22 pct of the available sunlight to electricity, compared with about 16 pct for silicon solar cells. Because of their higher energy efficiency, GaAs solar cells can be smaller than those constructed of silicon and still provide the same power to the satellite. Consequently, a satellite can carry a greater payload when GaAs is used as the solar cell material. GaAs is also more resistant to radiation than silicon; consequently, GaAs solar cells have a longer life in space environments (*1*).[2]

One defense application of optoelectronic GaAs is in night vision equipment. The GaAs component converts infrared radiation to visible light, enabling soldiers to see at night. Four layers of GaAlAs are epitaxially deposited on a GaAs substrate. The substrate and two of the layers are removed, yielding a thin GaAlAs film. Fabrication of these devices is closely controlled to prevent defects in the crystal structure. Even small imperfections in the night vision device cannot be tolerated.

Substitute materials are available for GaAs-based devices in many of the optoelectronic applications. Liquid crystal displays (LCDs), organic compounds that change their light reflection and refraction properties when a current is applied, are the most common substitute for LEDs. For example, LEDs have virtually been replaced by LCDs in one of their original applications–digital watches.

The principal competition for gallium-based laser diodes is from InP devices; because InP devices emit light at a longer wavelength than GaAs devices, they are suitable for fiber optic communications applications. However, InP technology is at a earlier stage of development than GaAs technology; thus, InP devices are more costly. Germanium- or silicon-based devices are the primary substitutes for gallium-based photodiodes. Competing materials for solar cells are silicon, copper indium diselenide, and cadmium telluride. Although not as efficient in thin-film solar cells as GaAs, they are generally less costly.

INTEGRATED CIRCUITS

Although ICs currently represent a smaller share of the GaAs market than optoelectronic devices, they are considered to have potential for greater growth. Two types of ICs are produced commercially–analog and digital. Analog ICs are designed to process signals generated by radar and military electronic warfare systems, as well as those generated by satellite communications systems. Digital ICs essentially function as memory and logic elements of computers.

Analog ICs

Analog or microwave ICs are used principally in defense applications. Although silicon technology is preferred for signals at frequencies of 3 GHz or less, such as those in television, radios, and computers, silicon operates too slowly at higher frequencies. For these higher frequencies, up to 30 GHz, GaAs microwave ICs are used. One type of GaAs IC, the monolithic microwave IC (MMIC), combines several discrete components on one chip and can perform functions that used to require bulky circuits consisting of vacuum tubes and waveguides.

One application of GaAs MMICs is in phased-array radar systems. With the development of the GaAs MMIC, the size of radar components can be decreased significantly, with improved signal-to-noise ratio. In phased-array radar, the antenna elements are fixed in a matrix in a single plane, rather than in a rotating dish, and are steered electronically to allow sky-borne objects to be individually identified. Because GaAs MMICs are small, the size of the antennas can be reduced significantly, perhaps enough to enable phased-array radar systems to fit on an airplane. Current phased-array radar systems are too large for this application.

Another defense application of GaAs MMICs is in expendable decoys designed to provide fighter aircraft with protection against radar-directed antiaircraft missiles. These decoys contain a small radar transmitter and receiver that, when ejected from an aircraft, begin transmitting the same frequency of radar energy as that reflected from the aircraft, although at a higher strength. Thus, a radar-directed missile would home in on the decoy, rather than the aircraft. Because of the small size of GaAs MMIC components in the radar, these decoys are only about 6 in long and 1 in in diameter.

GaAs MMICs are also a component of solid-state, phased-array jammers. These jammers can be surface-mounted on aircraft to receive and jam radar signals. With GaAs MMIC technology, the need for jamming pods is eliminated, providing space to carry additional weapons.

GaAs MMIC technology is still in its infancy, and many defense applications for MMICs are being developed. These military applications include space-based radar, missile seekers, "smart" munitions and other electronic warfare devices, and navigation and communications. GaAs MMIC applications may spread to the commercial sector, including direct broadcast satellite receivers and business communications equipment, such as cellular telephones.

Digital ICs

The first digital GaAs-based ICs were introduced into the U.S. market as "off-the-shelf" products in 1984. Consequently, their use in computer systems has been limited. In most cases, GaAs components are used in the high-speed supercomputers being developed. Because of the high cost of GaAs as compared with silicon, GaAs digital ICs are not expected to replace silicon ICs in most high-volume commercial applications, such as personal computers. The use of GaAs digital ICs will be confined to operations in which large quantities of data must be interpreted in a very short time, such as in weather forecasting and surveillance satellites. GaAs digital ICs

[2]Italic numbers in parentheses refer to items in the list of references at the end of this report.

also may be used in space-borne signal processing applications, such as those required for the implementation of Strategic Defense Initiative.

OTHER APPLICATIONS

Gallium is used in applications other than those in which its semiconductor properties are important. Gallium oxide is used in making some single-crystal "garnets" for special applications. As used in the electronics industry, the term "garnet" refers to compounds of mixed M_2O_3 metal oxides. Gallium gadolinium garnet (GGG) is used as the substrate for a bubble memory device. The single crystals are produced by conventional means, and an epitaxial layer is added that contains rare earth oxides. These rare earth oxides provide magnetic domains, or bubbles, that can be oriented to store information and moved, by an electric field, for information readout. Memory devices can be made with silicon materials, bubbles, or magnetic tape or disks. These three technologies compete on the bases of cost and size. Silicon devices are low cost and small, but they require power to retain information; otherwise the data are volatile and subject to loss. Although bubbles are costlier and disks are bulkier than comparable silicon devices, they are nonvolatile, which makes them attractive for certain applications. Although not commonly used in most computer applications, GGG bubble memories are suited to dirty environments and environments that are subject to wide fluctuations in temperature. Commercial applications for GGG bubble memories include petrochemical data collection and plant machine control. Gallium, scandium, and gadolinium oxides are being used as another, mixed-oxide, single-crystal garnet (GSGG). GSGG has demonstrated improved efficiency as a laser host with potential inertial fusion energy applications.

Small quantities of metallic gallium are used for low-melting-point alloys, for dental alloys, and as a component in some magnesium, cadmium, and titanium alloys. Gallium is also used in high-temperature thermometers and as a substitute for mercury in switches, because it has the longest liquid range of any element. Gallium has additional uses in glasses and mirror coatings.

PROPERTIES AND GRADES

GaAs has several properties that give it advantages over silicon in many applications. These advantages are particularly prominent in optoelectronic applications. When stimulated by an electric current, GaAs gives off either visible or infrared light; silicon only gives off energy in the form of infrared radiation or heat. This makes GaAs a useful material for fabricating LEDs and laser diodes, applications for which silicon cannot be used. Both GaAs and silicon can convert light to electrical energy, which makes them useful for photodiodes and solar cells, but GaAs can convert more of the available light to electrical energy, making it more energy efficient.

In IC applications, GaAs's properties make it especially appealing in defense applications. GaAs is about 10 times more resistant to radiation than silicon. This is essential in satellite operations in space, where components are exposed to damaging radiation from the sun. GaAs circuits also can operate at higher temperatures than can those of silicon–generally up to 350° C for GaAs compared with 275° C for silicon. Therefore, the need for bulky cooling equipment is reduced. Also, electrons move up to five or six times faster through GaAs than through silicon. This allows for faster operation of GaAs-based circuits, which will be of growing importance as defense applications become increasingly sophisticated and require split-second decision-making capabilities.

All of these properties make GaAs attractive, but GaAs has several drawbacks that limit its use only to those applications where its properties are crucial. The first of these drawbacks is its cost. Depending on the application, an ordinary GaAs wafer can cost $\$5/in^2$ to $\$25/in^2$–a 3-in-diameter, undoped, semi-insulating GaAs wafer would cost about \$185 to \$200, compared with \$12 for a 6-in-diameter silicon wafer.

The second drawback is that GaAs is much more difficult to fabricate than silicon. It is much more difficult to grow a single-crystal ingot from two elements than from one, especially when the arsenic tends to diffuse out of the melt at temperatures lower than that required for GaAs crystal growth. Consequently, GaAs wafers have more imperfections in the crystal structure than silicon wafers, which may adversely affect the electronic properties of a device constructed on the wafer. GaAs also has lower production yields than silicon. From ingot to usable wafers, GaAs has an effective yield of about 15 pct. GaAs wafers are also brittle and subject to breakage during

device fabrication, decreasing the effective yield still further.

Purity requirements for the raw materials to produce GaAs are stringent. For optoelectronic devices, the gallium and arsenic must be at least 99.9999 pct pure; for ICs, a purity of 99.99999 pct is required. These two purity levels are referred to by several names–99.9999-pct-pure gallium is often called 6-nines, 6N, or optoelectronic (opto) grade, while 99.99999-pct-pure gallium is called 7-nines, 7N, semi-insulating (SI), or IC grade. For 7N gallium, the total of the impurities must be less than 100 ppba. In addition to the difficulty of consistently producing material with such high purity, it is difficult to analyze for the small quantity of impurities. Certain impurities can cause more problems during GaAs production than others. The impurities 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 less than 1 ppba in both the gallium and arsenic. Lead, mercury, and zinc should be present in concentrations less than 5 ppba. Although aluminum, chlorine, and sodium are often present, each of their concentrations should be less than 10 ppba.

RESOURCES

Although gallium is as abundant in the Earth's crust as lead, it is widely disseminated and is rarely found in concentrations greater than 0.1 pct. Consequently, gallium is nearly always recovered as a byproduct during processing of ores or other materials to recover other metals. The principal materials in which gallium is found are bauxite, coal, phosphate ores, and sphalerite (zinc ore). Of these, gallium is currently commercially recovered during the processing of bauxite to alumina and the processing of sphalerite to zinc.

Bauxite generally is considered the most likely source of byproduct gallium, because gallium occurs in virtually all bauxites and is somewhat concentrated during the extraction of alumina from bauxite via the Bayer process. The gallium content of bauxite varies depending on the individual deposit, averaging about 50 ppm for the world. Bauxites containing high quantities of gallium, 70 to 80 ppm, are found in India, Suriname, and the United States. Table 1 shows an estimate of the world gallium reserves and reserve base available from bauxite, based on bauxite reserves and reserve base and the average gallium content of the bauxite in each country (*2*).

Although world gallium reserves of over 1 million mt are available from bauxite, much of this bauxite will not be mined for many decades, and only about 40 pct of the available gallium is recoverable with current technology. Table 2 presents a projection of the annual gallium capacity of each of the world's Bayer alumina plants, based on each plant's alumina capacity, sources of bauxite, bauxite-to-alumina ratio, and gallium content. Australia, Jamaica, the U.S.S.R., and the United States have the most potential for gallium recovery from bauxite.

Because gallium is not recovered at many alumina plants throughout the world, and because most of the gallium originally contained in the bauxite does not dissolve during the alumina extraction process, large quantities of gallium are discarded in the red mud residue. Although not currently considered a gallium resource material, the red mud residue represents a large potential gallium resource. Much of the residue is contained in tailings ponds near the alumina refineries and would be an easily accessible resource.

Zinc ores also represent a significant source of gallium, although not all zinc ores contain gallium. Sphalerite, a zinc sulfide mineral, generally contains detectable quantities of gallium, but little quantitative information is available to present an accurate assessment of the gallium potential of these ores. Based on the assumption that the average gallium content of sphalerite is 50 ppm, domestic sphalerite reserves of 21 million mt contain 1,050 mt of gallium. Total world reserves of 147 million mt of sphalerite may contain as much as 7,350 mt of gallium. The countries with the largest sphalerite reserves are Canada, the United States, and Australia. As with bauxite, much of this ore will not be mined for many decades and represents a long-term source of gallium.

Coal fly ash and phosphate flue dusts also contain gallium, but because of the availability of gallium from bauxite and sphalerite, it is unlikely that these materials would be used as principal sources of gallium, although technology to recover gallium from these materials has been developed.

Table 1. - Gallium reserves and reserve base[1]

Country	Bauxite reserves, 10^3 mt	Bauxite reserve base, 10^3 mt	Gallium content, pct	Gallium reserves,[2] mt	Gallium reserve base,[2] mt
Australia	4,440,000	4,600,000	0.006	106,560	110,400
Brazil	2,800,000	2,900,000	.005	56,000	58,000
Cameroon	680,000	800,000	.004	10,880	12,800
China	150,000	150,000	.006	3,600	3,600
Dominican Republic	30,000	45,000	.004	480	720
France	30,000	40,000	.003	360	480
Germany, Federal Republic of	2,000	2,000	.003	24	24
Ghana	450,000	560,000	.003	5,400	6,720
Greece	600,000	650,000	.003	7,200	7,800
Guinea	5,600,000	5,900,000	.003	67,200	70,800
Guyana	700,000	900,000	.005	14,000	18,000
Haiti	10,000	14,000	.004	160	224
Hungary	300,000	300,000	.003	3,600	3,600
India	1,000,000	1,200,000	.007	28,000	33,600
Indonesia	750,000	805,000	.004	12,000	12,880
Italy	5,000	5,000	.003	60	60
Jamaica	2,000,000	2,000,000	.006	48,000	48,000
Malaysia	15,000	15,000	.003	180	180
Mozambique	2,000	2,000	.003	24	24
Pakistan	20,000	20,000	.003	240	240
Romania	50,000	50,000	.003	600	600
Sierra Leone	140,000	160,000	.004	2,240	2,560
Spain	5,000	5,000	.003	60	60
Suriname	575,000	600,000	.008	18,400	19,200
Turkey	25,000	30,000	.003	300	360
U.S.S.R.	300,000	300,000	.005	6,000	6,000
United States	38,000	40,000	.007	1,064	1,120
Venezuela	320,000	350,000	.003	3,840	4,200
Yugoslavia	350,000	400,000	.003	4,200	4,800
Zimbabwe	2,000	2,000	.003	24	24
Other	200,000	200,000	.003	2,400	2,400
Total	21,589,000	23,045,000	NAp	[3]400,000	[3]430,000

NAp Not applicable.
[1]Reserve base includes reserves.
[2]Based on a 40-pct gallium recovery.
[3]Rounded.

Table 2. - World alumina plant capacities and gallium potential, yearend 1987

Company name	Plant location	Bauxite sources	Annual alumina capacity, 10^3 mt	Annual gallium potential, mt
Australia:				
Alcoa of Australia Ltd.	Kwinana, Western Australia	Australia	1,400	224
Do	Pinjarra, Western Australia	.. do	2,300	369
Do	Wagerup, Western Australia	.. do	570	116
Nabalco Pty. Ltd.	Gove, Northern Territory	.. do	1,100	161
Queensland Alumina Ltd.	Gladstone, Queensland	.. do	2,300	328
Worsley Alumina Pty. Ltd.	Worsley, Western Australia	.. do	1,000	204
Total Australia			8,670	1,402
Brazil:				
Alcan Aluminio do Brazil	Saramenha, Minas Gerais	Brazil	120	13
Alcoa Aluminio S.A.	Pocos de Caldas, Minas Gerais	.. do	180	19
Aluminio do Maranhao S.A.	Sao Luis, Maranhao	.. do	500	58
Cia Braziliera de Aluminio	Sorocabo, Sao Paulo	.. do	400	44
Total Brazil			1,200	134
Canada: Alcan Basic Raw Materials	Jonquiere, Quebec	Brazil, Guinea, Guyana.	1,225	73
China:				
Fushun Alumina Plant	Province of Liaoning	China	250	35
Guiyang Alumina Plant	Province of Guizhou	.. do	220	30
Hejin Alumina Plant	Province of Shanxi	.. do	200	28
Nanding Alumina Plant	Province of Shangdong	.. do	220	30
Tian Alumina Plant	Province of Shaanxi	.. do	130	18
Wenchang Alumina Plant	Province of Hainan	.. do	180	25
Total China			1,200	166
Czechoslovakia:				
ZNSP Kovohute Praha	Ziar nad Hronom	Hungary, Yugoslavia.	100	7
France:				
Aluminium Pechiney	Gardanne	France, Guinea	700	62
Do	La Barasse	.. do	340	30
Total France			1,040	92
Germany, Federal Republic of:				
Aluminum Oxid Stade GmbH	Stade	Australia, Guinea.	600	57
Martinswerk GmbH	Bergheim	Australia, Sierra Leone.	350	39
Vereinigte Aluminium Werke AG	Lippewerke, Lunen	Australia, Guinea	430	41
Do	Nabrewerke, Schwandorf	.. do	120	11
Total Federal Republic of Germany			1,500	148
Greece: Aluminium de Grece S.A.	Distommon	Greece	600	41
Guinea: Friguia Societe D'Economie	Kimbo	Guinea	700	43
Guyana: Guymine	Linden	Guyana	354	35
Hungary:				
Hungarian Aluminium Corp.	Ajka	Hungary	475	34
Do	Alamasfuzito	.. do	335	24
Do	Mosonmagyarovar	.. do	110	8
Total Hungary			920	66
India:				
Bharat Aluminium Co. Ltd.	Korba, Madhya Predesh	India	200	31
Hindustan Aluminium Corp. Ltd.	Renukoot, Utter Pradesh	.. do	160	25
Indian Aluminium Co.	Belgaun, Karnataka	.. do	160	25
Do	Muri, Bihar	.. do	72	11
Madras Aluminium Co. Ltd.	Mettur, Tamil Nadu	.. do	60	9
National Aluminium Co. Ltd.	Damamjodi, Orissa	.. do	800	122
Total India			1,452	223
Ireland: Aughinish Alumina Ltd.	Aughinish, Limerick County	Guinea	800	48

Table 2. - World alumina plant capacities and gallium potential, yearend 1987—Continued

Company name	Plant location	Bauxite sources	Annual alumina capacity, 10^3 mt	Annual gallium potential, mt
Italy:				
Aluminio Italia	Porto Marghera	Australia, Brazil, Guinea, Yugoslavia.	200	20
Eurallumina SpA	Porto Vesme, Sardinia	Australia, Guinea.	720	86
Total Italy			920	106
Jamaica:				
Alpart	Spur Tree	Jamaica	1,180	177
Clarendon Alumina Production Ltd.	Halse Hall, Clarendon	.. do	550	83
Jamaican Joint Venture	Ewarton, St. Catherine	.. do	566	85
Do	Kirkvine, Manchester	.. do	558	77
Total Jamaica			2,854	422
Japan: Nippon Light Metal Co.	Shimizu	Australia, Indonesia.	380	44
Romania:				
Alumina Enterprise	Oradea	Romania	250	17
Do	Tulcea	.. do	250	17
Total Romania			500	34
Spain: Aluminia Espanola S.A.	San Ciprian	Guinea	800	48
Suriname: Paranam Refinery Joint Venture.	Paranam	Suriname	1,352	234
Turkey: Etibank Alumina Plant	Seydisehir	Turkey	200	14
U.S.S.R.:				
Bogslav Aluminium	Northern Urals	U.S.S.R.	350	50
Dnjepr Aluminium	Zaporashye	U.S.S.R., Guinea, Yugoslavia, Hungary, Jamaica.	300	30
Nikolaev Alumina	Black Sea, South Ukraine	Guinea, Yugoslavia, Jamaica, Brazil, Guyana.	1,000	74
Novokuzneck Alumina	Kemerovo	U.S.S.R.	250	35
Pavlodar Alumina	Kazakhstan, Central Asia	.. do	500	71
Tikhvin Alumina	Leningrad	U.S.S.R., Guinea, Yugoslavia, Brazil, Jamaica.	350	35
Ural Aluminium	Urals	U.S.S.R.	250	35
Total U.S.S.R.			3,000	330
United States:				
Aluminum Co. of America	Point Comfort, TX	Guinea, Suriname.	1,210	125
Kaiser Aluminum & Chemical Corp.	Gramercy, LA	Jamaica	725	109
Reynolds Metals Co.	Corpus Christi, TX	Guinea, Brazil, Australia, Jamaica.	1,256	142
Total United States			3,191	376
Venezuela:				
Interamericana de Alumina C.A.	Puerto Ordaz, Orinoco	Guyana, Brazil, Suriname.	1,300	156
Yugoslavia:				
Energoinvest Aluminium	Bacevici, Mostar, Bih	Yugoslavia	280	19
Do	Zvornick, Vlasneica	.. do	600	42
Kombinat Aluminijuma Titograd	Titograd, Montenegro	.. do	280	19
Tvornica Lakih Metala	Obravac, Dalmatia	.. do	300	21
Unial Tovarna Glinice in Alumina	Kidricevo, Slovenia	Yugoslavia, Guinea.	140	9
Total Yugoslavia			1,600	110
World total			35,858	4,352

RECOVERY TECHNOLOGY

GALLIUM RECOVERY FROM BAUXITE

Throughout the world, alumina is recovered from bauxite by the Bayer process. In this process, alumina is extracted from bauxite through digestion with a hot caustic solution. After the slurry is cooled and solid residue is separated from the aluminum-containing liquor, the solution is seeded with alumina trihydrate crystals to precipitate the dissolved aluminum as alumina trihydrate. Alumina trihydrate is separated from the solution and calcined to produce alumina, while the caustic solution is recycled to the bauxite digestion step.

Because gallium is chemically similar to aluminum, it tends to remain with aluminum during processing. When the aluminum is extracted during digestion, gallium is also extracted. Gallium is not removed from the solution during subsequent processing steps, and because the solution is recycled, gallium builds up to an equilibrium concentration of 100 to 125 ppm. When gallium recovery is desired, a bleed stream is separated from the caustic solution before it is recycled to the digestion step. Crude gallium metal, 97.0 to 99.9 pct pure (3N), is recovered by two principal processes–the Beja process and the de la Breteque process. Simplified flowsheets for these processes are shown in figures 1 and 2.

In the Beja process, carbon dioxide is injected into the bleed solution to precipitate aluminum not recovered in the Bayer process as alumina trihydrate. The trihydrate is separated from the solution, and the gallium-containing solution is carbonated again. In the second carbonation, a gallium precipitate, containing between 0.3 and 1 pct gallium, is recovered. Both of the carbonation steps are carefully controlled so that about 90 pct of the aluminum is removed during the first carbonation and 90 pct of the gallium is precipitated during the second carbonation. After the gallium precipitate is separated from the solution, which is recycled to the Bayer process, the precipitate is dissolved in a caustic solution to increase the gallium-to-aluminum ratio. This solution is electrolyzed to recover crude gallium as a liquid. The spent solution is recycled to the Bayer process (*3*).

In the de la Breteque process, a bleed stream from the Bayer process is concentrated by evaporation to increase the gallium concentration. Concentrated solution is directly electrolyzed using a highly agitated mercury cathode. The agitation allows the gallium to form an amalgam with the mercury. When the gallium concentration reaches about 1 pct in the amalgam, it is drawn off and leached with a caustic solution. This yields a concentrated gallium solution from which crude gallium can be recovered by electrolysis (*4*).

Because mercury losses are significant owing to the high level of cathode agitation in the de la Breteque process, a modification to the process was developed by Vereinigte Aluminium Werke AG (VAW) of the Federal Republic of Germany. Rather than preparing a gallium-mercury amalgam by electrolysis, a sodium-mercury amalgam is prepared by electrolyzing the caustic solution with a mercury cathode. Gallium is then extracted by a cementation process as the gallium in solution replaces the sodium in the amalgam. Subsequent gallium recovery follows the same steps as in the de la Breteque process.

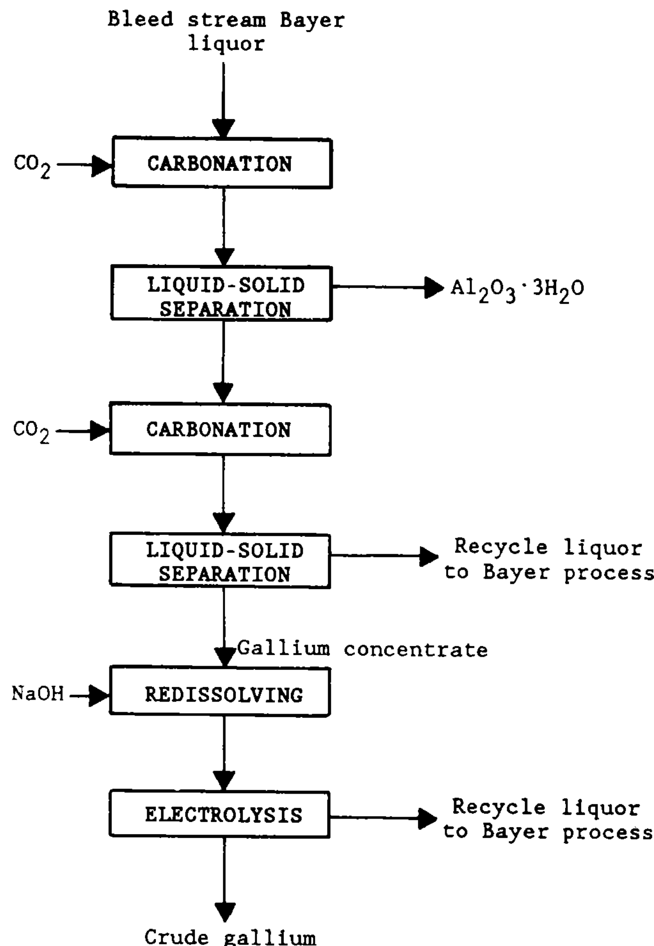

Figure 1.–Beja process for recovering crude gallium from Bayer liquors.

Although the de la Breteque process and the VAW modification are the most commonly used processes, several companies have developed proprietary recovery techniques that they claim are less costly than conventional processes. Rhône-Poulenc S.A. uses a liquid-liquid extraction technique at its plant in France to recover gallium from Bayer liquors. Sumitomo Chemical Co. Ltd. of Japan uses an unidentified absorbent to extract gallium directly from Bayer liquor.

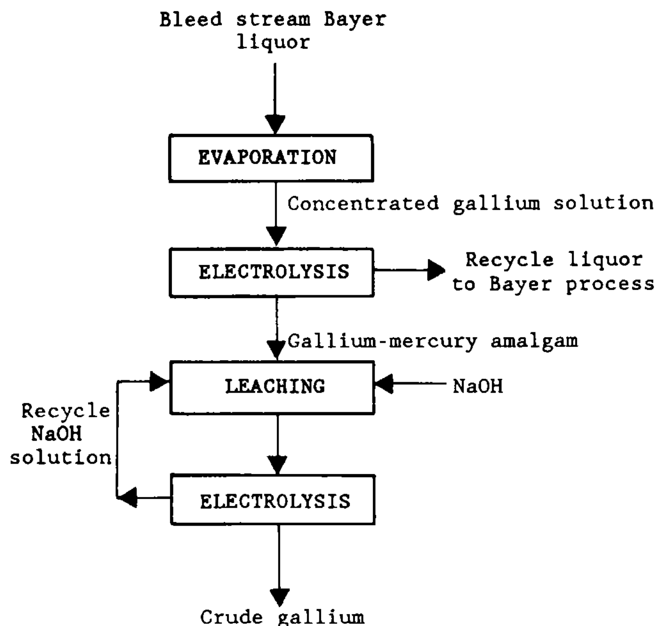

Figure 2.—de la Breteque process for recovering crude gallium from Bayer liquors.

GALLIUM RECOVERY FROM ZINC ORE

Dowa Mining Co., the only company that currently recovers gallium from zinc ore, uses an electrolytic method for producing zinc. In recovering zinc by this method, a roasted zinc concentrate is leached with sulfuric acid to produce a zinc sulfate solution, which is neutralized to remove impurities. Impurities that precipitate from the zinc sulfate solution include gallium, aluminum, and iron. Leaching this residue with a caustic solution extracts the gallium, along with the aluminum and iron impurities. After the remaining residue is separated from the gallium-containing solution, the solution is neutralized to precipitate the metal hydroxides. The hydroxide solids are leached with hydrochloric acid to dissolve gallium and aluminum, and the gallium is separated from the aluminum in solution by solvent extraction with ether. Distillation of the ether solution yields a gallium-rich residue that still contains some iron, which is removed by treating the residue with a strong caustic solution to extract the gallium, while leaving the iron as a solid. Iron residue is filtered from the gallium-containing solution, and crude gallium is recovered by electrolysis. A simplified flowsheet for this process is shown in figure 3.

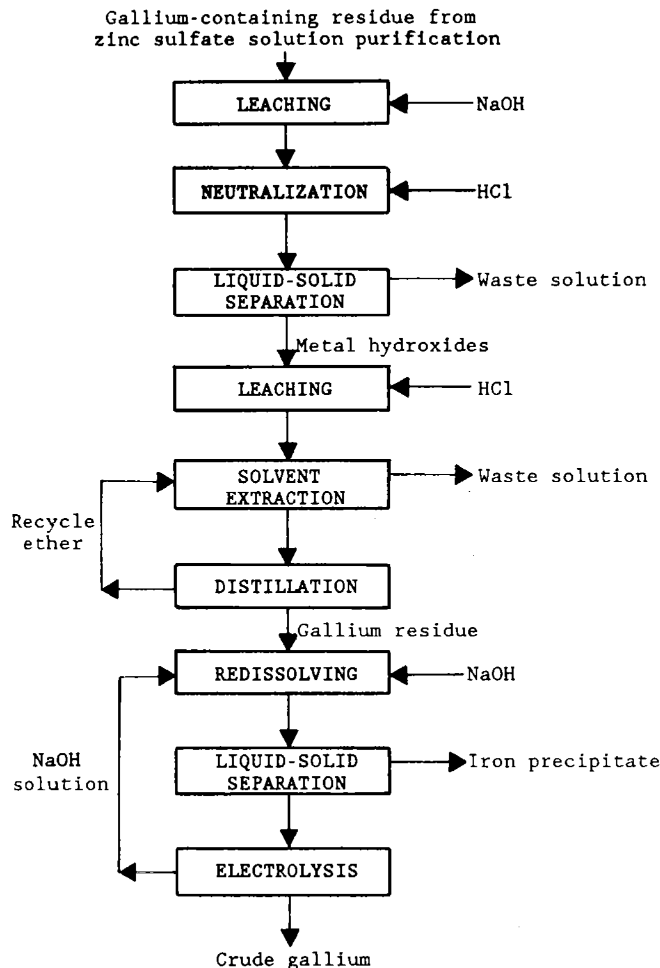

Figure 3.—Gallium recovery from zinc ore.

GALLIUM RECOVERY FROM OTHER SOURCES

Other sources of gallium that have been investigated include phosphate flue dust, coal fly ash, aluminum smelter flue dusts, and iron oxide minerals found in Utah. The only sources that have been commercially treated to recover gallium are the minerals in Utah and aluminum smelter flue dusts. In 1986, St. George Mining Corp., a subsidiary of Musto Explorations Ltd., began recovery of gallium from an abandoned copper mine near St. George, UT. Although much of the copper had been mined, the remaining iron oxide minerals contained an average of 0.042 pct gallium. Because this source material is different from bauxite or zinc ore, a new processing technique was developed, as shown in figure 4.

Crushed ore is leached with sulfur dioxide gas, a sulfuric acid solution, and fluorspar to extract gallium, along with germanium, copper, iron, and zinc. After the insoluble impurities are separated, copper is cemented by the addition of iron and separated from the gallium-containing solution. Dissolved germanium is precipitated as a sulfide by injection of hydrogen sulfide gas into the solution, and the precipitate is removed and treated to recover germanium dioxide. The solution, containing gallium, zinc, and iron, undergoes solvent extraction, where the gallium and zinc are extracted into the organic solution; the iron remains in the aqueous phase. Gallium and

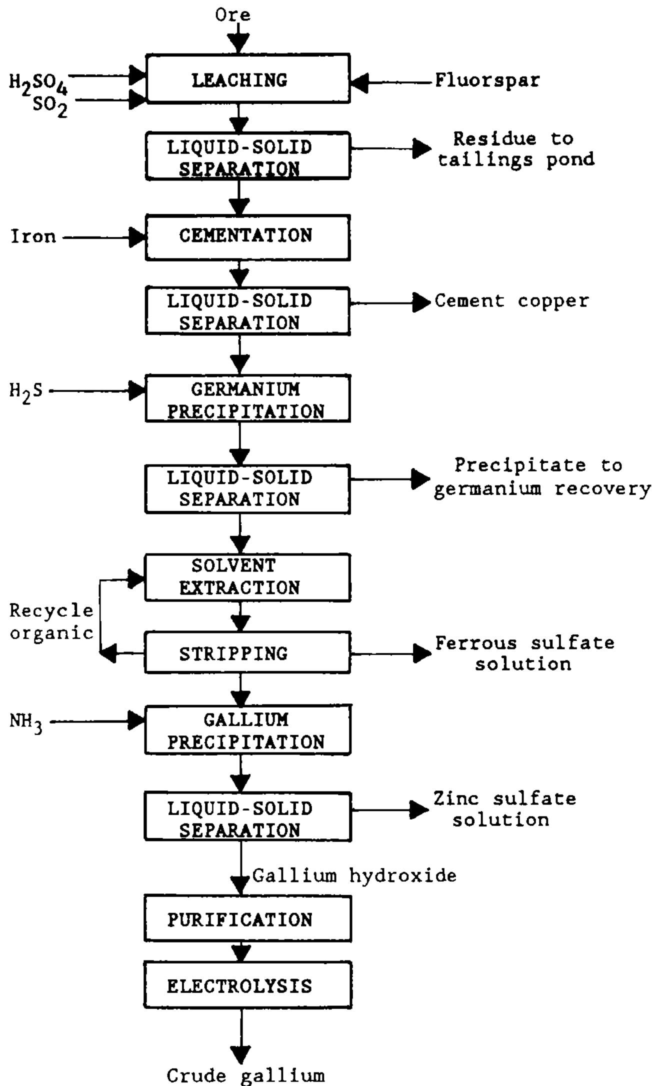

Figure 4.—Gallium recovery from Musto Explorations Ltd.'s mine near St. George, UT.

zinc are stripped from the organic phase, and ammonia is injected into the stripped solution to precipitate gallium hydroxide. Gallium hydroxide precipitate is separated from the zinc solution and purified, and 99.999-pct-pure (5N) gallium metal is recovered by electrolysis. The electrolytic technology used at Musto's plant is proprietary technology licensed from Cominco Ltd.

In July 1987 Elkem A/S of Norway began producing crude gallium using aluminum smelter flue dust as a source material. Dusts generated at two smelters in Mosjoen and Tyssedal are blended to yield material with the following average concentration: Carbon, 33 pct; fluorine, 17 pct; oxygen, 17 pct; aluminum, 13 pct; sodium, 9 pct; iron, 6 pct; sulfur, 3 pct; calcium, 1.5 pct; and gallium, 0.5 pct. Leaching the flue dust with hydrochloric acid extracts the gallium. Solids are filtered from the liquid phase and mixed with portland cement before disposal. The liquid phase undergoes a series of solvent extraction stages to separate gallium from dissolved impurities. After cleaning and stripping, crude gallium is recovered by electrolysis of the water phase. A simplified flowsheet for this process is shown in figure 5.

GALLIUM PURIFICATION

For most applications, purity requirements for gallium are either 6N or 7N. Crude gallium is purified in essentially two steps–the first step produces 99.99-pct-pure (4N) gallium, and the second produces 6N to 7N metal.

Many of the impurities in crude gallium occur in the surface oxide or as finely dispersed phases in the metal. Liquid gallium filtration and heating under vacuum remove these types of impurities. Metallic impurities can be reduced to less than 0.01 pct, producing 4N gallium, by sequential washing with hydrochloric acid. Another method that can be used is electrolytic refining, which involves anodic dissolution of gallium in an alkaline solution, and then deposition at a liquid gallium cathode.

The principal method used to produce 6N and 7N metal is gradual crystallization of molten gallium. In this process, impurities remain in the liquid phase and do not contaminate the gallium crystal. Crystallization is repeated until gallium of the desired purity is obtained. Another method of producing high-purity gallium is to convert the gallium to a halide compound, such as gallium trichloride, which is then zone-refined. High-purity gallium is recovered by electrolysis of the halide compound.

GALLIUM ARSENIDE FABRICATION

GaAs single crystals are more difficult to fabricate than those of silicon. With silicon, only one material needs to be controlled, whereas with GaAs, a one-to-one 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 a loss of arsenic, which would result in the formation of an undesirable gallium-rich crystal, GaAs ingots are grown in an enclosed environment to contain the arsenic.

Two basic methods are used to fabricate GaAs single-crystal ingots-the boat-growth, horizontal Bridgeman (HB) or gradient freeze technique, and the liquid-encapsulated Czochralski (LEC) technique. Ingots produced by the HB method are D-shaped and have a typical cross-sectional area of about 2 in^2. By contrast, single-crystal ingots grown by the LEC method are round and are generally 3 in in diameter, with a cross-sectional area of about 7 in^2.

In HB growth, gallium and arsenic in the proper ratio are placed in one end of a silicon dioxide (quartz) or pyrolytic boron nitride boat. A seed GaAs crystal is contained at the other end of the boat. The boat is placed in a sealed quartz tube, which is evacuated to a very low pressure. The tube is placed in a multiple-zone furnace, where the gallium and arsenic react to form GaAs. The

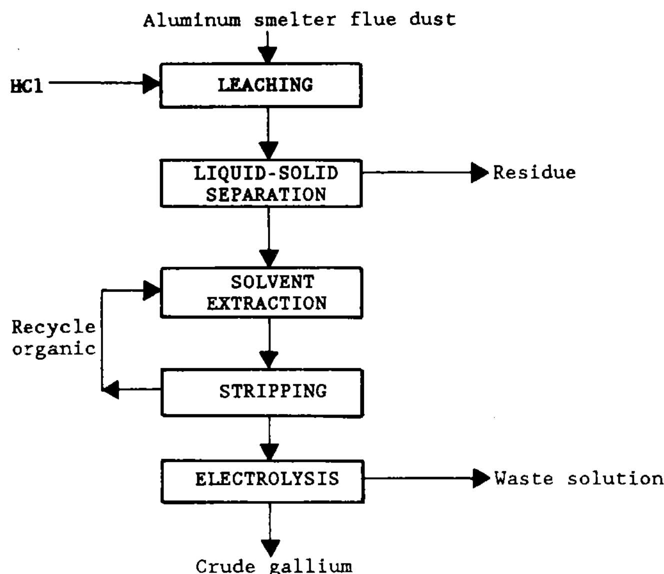

Figure 5.—Elkem A/S process for recovering gallium from aluminum smelter flue dust.

compound is heated to 1,240° C, the melting point of GaAs. The GaAs melt is slowly cooled from the seed end, resulting in single-crystal growth. In the LEC method of crystal growth (fig. 6), carefully weighed pieces of gallium and arsenic are melted in a pressurized vessel (crystal puller). The GaAs melt is contained in a crucible constructed of either high-purity quartz or pyrolytic boron nitride. The melt is covered with a layer of boric oxide, which retards arsenic loss from the melt by sublimation. A seed crystal is lowered through the boric oxide into the melt and slowly withdrawn as both the seed and crucible are rotating.

Each of these methods produces GaAs ingots with particular advantages and disadvantages. Crystals formed by the boat-growth method are particularly suitable for optoelectronic applications because their structure is highly perfect with respect to dislocations. Optoelectronic devices also require crystals with a high doping concentration, which boat-grown crystals readily provide, because the silicon dissolved from the quartz boat contributes to crystal doping. This latter benefit becomes a problem if semi-insulating GaAs crystals for ICs are being produced. The silicon impurities are called shallow donors, or N-type dopants. To compensate for these impurities, either a controlled quantity of gallium oxide can be added to the melt, or chromium, a deep acceptor or P-type dopant, can be added. Crystal growth also can be accomplished in a boron nitride container, which eliminates any contact with silicon-containing material during growth. The shape of the HB-grown ingot makes it inconvenient for subsequent wafer processing, because automated wafer processing systems are designed to handle round wafers. LEC-grown ingots generally contain more crystal structure defects, i.e., they have higher dislocation densities, than HB-grown ingots. This affects the electronic properties of the device constructed on the GaAs. Dislocation densities in HB wafers normally run between 500 and 20,000 per square centimeter; those in LEC wafers can be as large as 100,000 per square centimeter. Because chips are batch processed, wafer by wafer, the larger the wafer, the more chips per wafer, and the lower the cost per chip. A 3-in-diameter LEC-grown wafer can yield more of the same-size chips than a 2- by 1.5-in HB wafer. Conversely, the capital costs for an HB system are significantly less than those for an LEC system.

After the ingots are grown, the ends are cut off, and the ingots are shaped by grinding the edges. Ingots are then sliced into wafers (fig. 7). Wafers go through several stages of surface preparation, polishing, and testing before they are ready for device manufacture or epitaxial growth. Wafer preparation steps are done in a clean room and with minimal contact to avoid introducing surface contaminants. In LEC growth, the effective yield from starting material to finished wafers is currently less than 15 pct.

Pure GaAs is semi-insulating, which means that it is not a conductor of electricity. In order for GaAs to conduct electricity, a small number of atoms of another element must be incorporated into the GaAs crystal structure. This is called doping. These atoms act as electron donors or electron acceptors. Electron donor atoms have one more electron than the atoms that they are replacing, and this electron is free to move within the crystal as an electrical charge carrier. Electron acceptors have one less electron than the atoms they are replacing and behave as positively charged particles to serve as electrical charge carriers (5).

To manufacture devices from GaAs wafers, the wafers must be doped with another metal or metals. Normally, this is accomplished either by ion implantation or by some type of epitaxial growth. Because GaAs is a semi-insulating substrate, no special isolation areas are required to separate each device fabricated on the chip. This results in more compact, higher density circuits, which add to GaAs's speed advantage.

In ion implantation, ions of another metal are implanted into specific areas of the semi-insulating GaAs to make those areas electronically active. Areas of the chip that are to remain semi-insulating are covered with a photoresist mask before ion implantation. The process of ion implantation may be repeated several times with different metals on different areas of the chip, depending on the type and complexity of the device being manufactured. After ion implantation, the GaAs must be annealed at about 850° C in order to activate the implanted dopants and remove crystal damage incurred during implantation. When annealing, as in crystal growth, several techniques, including encapsulation of the chip, are used to prevent arsenic losses at the elevated temperature. After doping, optoelectronic device or IC manufacture can be completed through deposition of layers of metals and insulators by various techniques.

A similar technique, called ion cluster beam, is not as frequently used as ion implantation. In this technique, ions are grouped together and implanted into the wafer at

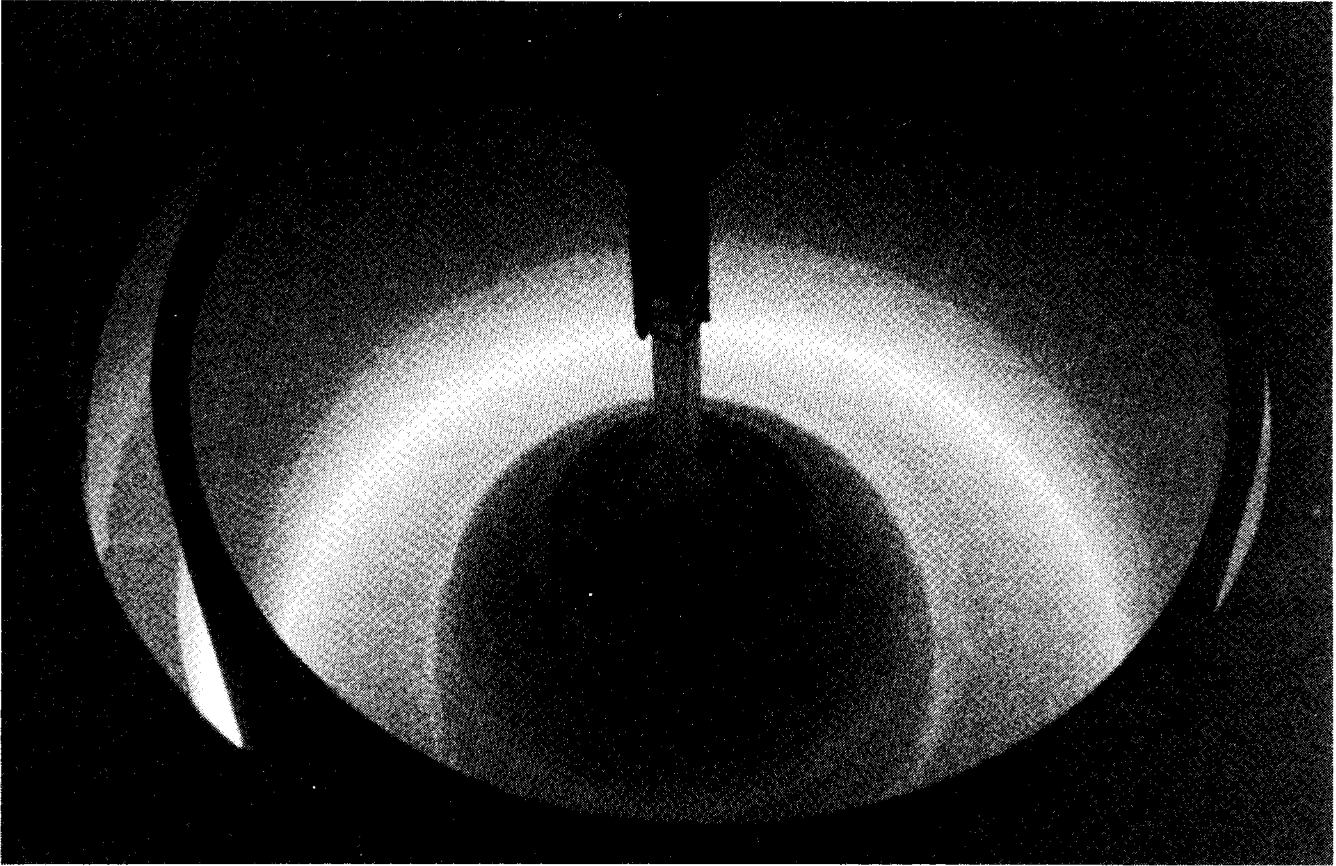

Figure 6.—GaAs ingot growing in LEC furnace (Courtesy Morgan Semiconductor Div. of Ethyl Corp.)

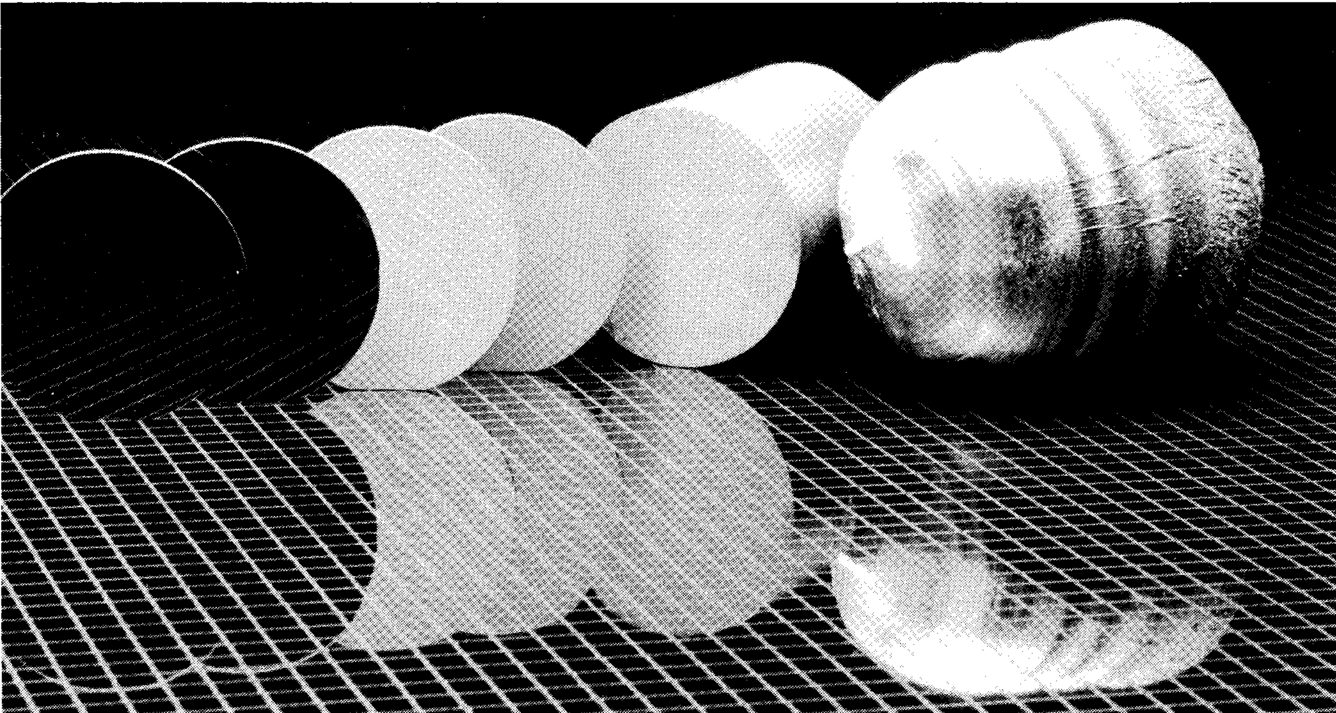

Figure 7.—LEC-grown GaAs ingot and wafers (Courtesy Morgan Semiconductor Div. of Ethyl Corp.)

lower speeds than used in ion implantation. This process is reported to result in less damage to the crystal structure.

The deposition of an epitaxial layer is another means of creating electronically active regions on the GaAs substrate. There are four principal methods for growing epitaxial layers–liquid-phase epitaxy (LPE), vapor-phase epitaxy (VPE), metal-organic chemical vapor deposition (MOCVD), and molecular beam epitaxy (MBE). LPE is an earlier method of epitaxy that is generally not considered suitable for complex semiconductor production because it cannot be as precisely controlled as the other three techniques. In LPE, the substrate wafer is contained in a graphite boat within a quartz furnace tube, where it is contacted with solutions containing the metals to be deposited. Cooling the solution causes the metals to precipitate on the substrate. LPE produces relatively thick epitaxial layers, and the boundaries between layers are gradual rather than sharply defined.

Two methods of VPE are used to grow epitaxial layers on a GaAs substrate–the hydride method and the chloride method. In VPE, GaAs substrates are mounted in a reactor. To make GaAsP epitaxial layers, two gaseous streams are introduced into the reactor. In the hydride process, one gas stream combines arsine (AsH_3) and phosphine (PH_3) with a hydrogen carrier gas; the other gas stream is a hydrochloric acid gas that has been passed over a gallium reservoir to form gallium trichloride, and that also is mixed with a hydrogen carrier gas. Dopants are added to the gas streams if necessary. Gallium trichloride reacts with the AsH_3 and PH_3 gases to deposit a GaAsP layer on the substrate. In the chloride process, arsenic trichloride and phosphorus trichloride gases are substituted for AsH_3 and PH_3. VPE technology can coat multiple wafers at the same time, and the layer thickness, molecular composition, and dopant concentration can be more closely controlled than with LPE.

In MOCVD, wafers are placed in a quartz reactor, maintained at atmospheric or slightly reduced pressure and at a temperature between 650° and 750° C. Metals to be deposited are in the forms of gases that chemically combine on the heated substrate. For example, to prepare a GaAlAs layer, gallium and aluminum are present in the form of organic gases, generally trimethyl or triethyl gallium and aluminum [$(CH_3)_3Ga$ or $(C_2H_5)_3Ga$ and $(CH_3)_3Al$ or $(C_2H_5)_3Al$] in a hydrogen carrier gas. Arsenic is in the form of AsH_3 in the hydrogen carrier gas. Dopants may also be added. The flow rates of these gases are carefully controlled. As the gases mix in the reactor and contact the hot wafers, they react to form GaAlAs and methane or ethane, and the GaAlAs deposits on the substrate wafers.

With MBE, the GaAs substrate is mounted on a heating block in a reactor maintained under a vacuum, along with effusion cells containing the elements to be deposited. For a GaAlAs layer, the effusion cells would contain gallium, aluminum, arsenic, and dopants. The elements are heated to temperatures that cause them to evaporate. By precise opening and closing of mechanical shutters in front of the effusion cells, the concentration of each element as it deposits can be carefully controlled.

With both MOCVD and MBE, the process may be repeated to build many thin layers of materials with differing compositions. After the epitaxial layers are deposited, device manufacture can be completed through deposition of metallic and insulating layers (fig. 8).

As with crystal growth methods, both MOCVD and MBE have advantages and disadvantages. MOCVD can coat multiple wafers at a time, whereas MBE systems can coat only one. MBE requires a vacuum, while MOCVD can be performed at atmospheric pressure. The cost of MOCVD equipment is approximately one-third the cost of MBE equipment ($250,000 compared with $800,000). MBE provides the most precise control over the composition and thickness of the epitaxial layers, and it also provides the greatest reproducibility. MOCVD uses AsH_3 gas, which requires a room equipped with safety equipment to prevent the toxic gas from escaping.

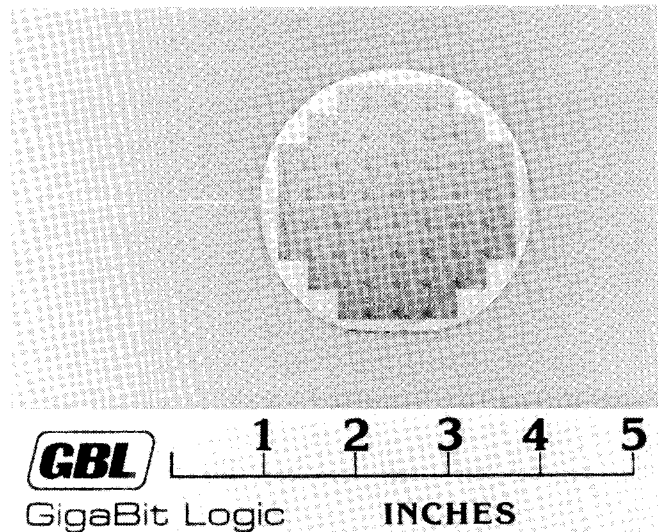

Figure 8.–GaAs wafer with devices (Courtesy GigaBit Logic Inc.)

SECONDARY RECOVERY

Because of the low yield in processing gallium to optoelectronic devices or ICs, substantial quantities of new scrap are generated during the various processing stages. These wastes have varying gallium and impurity contents, depending upon the processing step from which they result. GaAs-based scrap, rather than metallic gallium, represents the bulk of the scrap that is recycled. During the processing of gallium metal to a GaAs device, waste is generated during the GaAs ingot formation. If the ingot formed does not exhibit single-crystal structure or if it contains excessive quantities of impurities, it is considered to be scrap. Also, some GaAs remains in the reactor after the ingot is produced and may be recycled. During the wafer preparation and polishing stage, significant quantities of wastes are generated. Before wafers are sliced from the ingot, both ends of the ingot are cut off and discarded, because impurities are concentrated at the tail end of the ingot and crystal imperfections occur at the seed end. These ends represent up to 25 pct of the weight of the ingot. As the crystal is sliced into wafers, two types of wastes are generated–saw kerf, which is essentially GaAs sawdust, and broken wafers. When the wafers are polished with an abrasive lapping compound, a low-grade waste is generated. During the epitaxial growth process, various wastes are produced, depending on the growth method used. In LPE, metallic gallium contaminated with arsenic and dopant metals results, and in VPE, exhaust gases containing GaAs are produced. Because GaAs is a brittle material, wafers may break during the fabrication of electrical circuitry on their surfaces. These broken wafers also may be recycled.

Gallium content of these waste materials ranges from less than 1 pct to 99.99 pct. LPE wastes normally have the highest gallium content, 98 to 99.99 pct. Ingot ends and wafers broken during processing generally contain 39 to 48 pct gallium, VPE exhaust gases contain 6 to 15 pct gallium, saw kerf contains up to 30 pct gallium (wet basis), and lapping compound wastes contain less than 1 pct gallium. These wastes are contaminated with small quantities of many impurities, the most common being aluminum oxide, copper, chromium, germanium, indium, silicon, silicon carbide, tin, and zinc. Wafers broken during the fabrication of electrical circuitry also contain gold and silver impurities. In addition to metallic impurities, the scrap may be contaminated with materials introduced during processing such as water, silicone oils, waxes, plastics, and glass.

In processing GaAs scrap, the material is crushed, if necessary, and then dissolved in a hot acidic solution. This acid 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 electrolyzed to recover 3N to 4N gallium metal. This metal may be refined to 6N or 7N gallium by conventional purification techniques if desired.

Some GaAs manufacturers recycle their own scrap, or scrap may be sold to metal traders, to a company that specializes in recycling GaAs, or to the GaAs manufacturer's gallium supplier, who can recover the gallium and return it to the customer. Generally the prices commanded by GaAs scrap parallel the price fluctuations of 4N gallium metal. Also, prices are dependent on the type and gallium content of the scrap; saw kerf sells for a lower price than ingot scrap, which in turn sells for a lower price than metallic (LPE) scrap.

Although GaAs scrap is an important component of the gallium materials flow throughout the world, it cannot be considered an additional long-term source of world gallium supply. GaAs scrap that is recycled is new scrap, which means that it has not reached the consumer as an end product and is present only in the closed-loop operations between the companies that recover gallium from GaAs scrap and the wafer and device manufacturers. Because this closed loop occasionally crosses international boundaries, it is difficult to distinguish between gallium recovered from scrap and virgin gallium when evaluating the gallium supply of an individual country. For example, GaAs scrap generated in the United States and Canada may be processed to recover 4N gallium in Canada. The 4N gallium is shipped to Switzerland for refining to 7N gallium, which is then exported to the United States. In this situation, the gallium received in the United States from Switzerland appears to be a new source of supply, while in fact a portion of this gallium originated as GaAs scrap from the United States.

WORLD SUPPLY AND DEMAND

Little information is published detailing gallium production and trade data. The United States and Japan are the only countries for which detailed data are available. Also in many cases, no distinction is made in published figures between virgin, recycled, and purified gallium. As an example, the United States ships some GaAs scrap to the Federal Republic of Germany for gallium recovery, and the recovered gallium is returned to the United States. This gallium may be counted twice as a part of the domestic supply. Or, one country recovers virgin gallium and ships it to a second country for refining to 7N gallium. Each country may count this as production, thus doubling the quantity of gallium that appears to be available. Consequently, determination of gallium supply-demand figures is subject to significant interpretation.

PRODUCTION

Tables 3 and 4 show estimates of both primary and secondary gallium production. These figures were derived from U.S. production data, published by the Bureau of Mines; U.S. import data, supplied by the Department of Commerce; and production and import data for Japan, published in Roskill's Letter From Japan. Because most of the world's gallium demand centers in Japan and the United States, these sources are believed to provide data on about 85 pct of the gallium produced in the world.

TRADE

Import data for the United States and Japan are shown in tables 5 and 6. Historically, the United States has received most of its gallium from France, the Federal Republic of Germany, and Switzerland, while Japan's principal import sources have been China, France, and the Federal Republic of Germany. No data are published separately detailing gallium exports from the United States, Europe, or Japan. It is believed that no significant quantities of gallium are exported from either the United States or Japan, but significant trade in GaAs occurs. Some GaAs scrap is exported from the United States to the Federal Republic of Germany for gallium recovery, and Japan is believed to export significant quantities of GaAs substrate wafers to the United States. However, because the value of these items is very small when the value of the entire U.S. trade is considered, they are not classified separately. So the trade patterns of these materials cannot be quantitatively determined.

In addition to gallium metal and GaAs trade, the United States imports many of its consumer electronics goods and automobiles. Many of these items, such as compact disk players, televisions, calculators, and video cassette recorders, contain GaAs components in the form of LEDs and laser diodes. Here again, significant quantities of gallium compounds may be imported, but cannot be quantitatively determined.

DOMESTIC DEMAND

U.S. supply-demand relationships, shown in table 7, indicate that most of the domestic demand for gallium has been supplied by imports. Before 1983, the Aluminum Co. of America (Alcoa) and Eagle-Picher Industries Inc. recovered primary gallium in the United States. But after 1983, no primary gallium was produced until 1986, when Musto Explorations began recovering a small quantity of gallium from its mine in Utah.

Over 90 pct of the gallium consumed in the United States is classified as "instruments." This category includes gallium consumed in optoelectronic devices, in ICs, and in some research and development activities. The remainder, classified as "other," consists of gallium consumed in other research and development activities and in specialty alloys. Optoelectronic devices represent most of the gallium demand in the United States.

Table 3. - World primary gallium production[e]

(Kilograms)

Country	1980	1981	1982	1983	1984	1985	1986	1987
China	3,000	3,400	2,600	5,100	3,500	5,000	6,000	6,000
Czechoslovakia	500	1,650	1,700	2,000	2,500	3,300	3,000	3,200
France	4,300	4,600	3,700	7,000	8,500	9,500	15,500	14,000
Germany, Federal Republic of	2,300	3,000	4,000	5,300	6,000	5,500	7,000	7,000
Hungary	1,500	1,500	2,000	3,000	3,000	2,800	3,200	3,000
Japan	3,000	3,000	3,000	3,000	10,000	10,000	10,000	5,000
Norway	0	0	0	0	0	0	0	500
United States	3,000	1,500	1,560	0	0	[1]0	[1]750	W
Total	17,600	18,650	18,560	25,400	33,500	36,100	45,450	[2]38,700

[e]Estimated. W Withheld to avoid disclosing individual company proprietary data.
[1]Reported figure.
[2]Excluding U.S. production.

Table 4. - World secondary gallium production [e] [1]

(Kilograms)

Country	1980	1981	1982	1983	1984	1985	1986	1987
Canada	0	0	0	0	0	0	0	5,000
Germany, Federal Republic of	500	500	700	1,000	2,100	1,500	1,500	1,500
Japan	3,000	5,000	4,000	5,000	7,000	4,000	9,000	7,000
United Kingdom	200	300	800	1,000	1,000	1,000	1,500	1,500
United States	0	0	0	0	0	0	0	2,400
Total	3,700	5,800	5,500	7,000	10,100	6,500	12,000	17,400

[e]Estimated.
[1]New scrap only.

Table 5. - U.S./gallium imports for consumption, by country

(Kilograms)

Country	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987
Belgium-Luxembourg	0	0	0	0	200	0	0	0	55	0	0
Canada	276	75	450	1,449	589	379	279	1	3	98	107
China	0	0	0	409	916	0	500	400	0	0	0
Congo	0	0	0	0	0	0	0	0	10	0	0
Czechoslovakia	0	0	53	0	0	0	0	0	0	0	0
France	0	0	0	232	386	480	829	2,449	1,563	8,231	6,364
Germany, Federal Republic of	774	748	218	561	585	1,448	918	1,554	1,423	2,740	1,215
Hungary	0	37	59	0	0	0	0	168	0	17	0
India	0	0	0	0	10	0	0	0	0	0	0
Italy	349	0	0	0	98	0	0	1	0	0	13
Japan	0	0	41	13	0	48	146	89	105	123	451
Malaysia	0	100	0	0	2	0	0	5	40	0	0
Netherlands	0	0	41	0	0	0	0	131	50	0	0
New Zealand	0	0	0	0	0	0	0	132	0	0	0
Singapore	0	0	0	0	0	0	0	0	0	0	21
Spain	0	0	0	0	0	148	0	0	0	0	0
Suriname	0	0	0	0	0	0	0	0	30	0	96
Sweden	0	0	0	0	1	0	0	0	201	5	0
Switzerland	1,485	2,628	5,498	3,444	2,679	2,429	4,154	4,088	4,268	5,640	4,081
Taiwan	0	0	0	11	0	0	0	0	50	0	0
United Kingdom	0	133	41	56	70	267	468	651	163	348	142
Total	2,884	3,721	6,401	6,175	5,536	5,199	7,294	9,669	7,961	17,202	12,490

Source: U.S. Department of Commerce.

Table 6. - Japanese/gallium imports, by country

(Kilograms)

Country	1980	1981	1982	1983	1984	1985	1986	1987
Canada	0	0	0	0	0	0	300	300
China	2,500	2,400	2,600	4,600	2,800	4,000	5,100	2,000
Czechoslovakia	0	500	1,260	480	900	2,285	450	1,100
France	10	2,000	1,400	2,800	3,100	5,264	2,700	5,600
Germany, Federal Republic of	1,200	1,800	2,100	3,720	5,450	3,200	4,200	4,900
Hungary	10	600	1,600	2,300	1,500	1,800	750	1,500
Switzerland	1,400	300	120	100	85	50	100	740
U.S.S.R.	0	0	0	200	0	0	0	0
Total	5,120	7,600	9,080	14,200	13,835	16,599	13,600	16,140

Source: Roskill's Letter From Japan and Rare Metals News.

Table 7. - Gallium supply-demand relationships, 1977-87

(Kilograms)

	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987
WORLD PRODUCTION											
United States	W	[e]5,500	[e]2,600	[e]3,000	[e]1,500	[e]1,560	[e]0	[e]0	0	750	W
Rest of world	W	[e]6,650	[e]9,500	[e]14,600	[e]17,150	[e]17,100	[e]25,400	[e]33,500	[e]36,100	[e]44,700	[e]38,700
Total[e]	12,420	12,200	12,100	17,600	18,650	18,660	25,400	33,500	36,100	45,450	[1]38,700
COMPONENTS AND DISTRIBUTION OF U.S. SUPPLY											
Components of U.S. supply:											
Production	W	[e]5,500	[e]2,600	[e]3,000	[e]1,500	[e]1,560	[e]0	[e]0	0	750	W
Imports	2,884	3,721	6,401	6,175	5,536	5,199	7,294	9,669	7,961	17,202	12,490
Industry stocks, Jan. 1	W	[e]1,950	[e]2,000	[e]1,800	[e]1,900	[e]1,900	[e]1,855	1,830	926	1,206	813
Total	11,054	11,221	[e]11,001	[e]10,975	8,936	8,659	[e]9,149	11,499	8,887	19,158	W
Distribution of U.S. supply:											
Industry stocks, Dec. 31	[e]1,950	[e]2,000	[e]1,800	[e]1,900	[e]1,900	[e]1,855	1,830	926	1,206	813	732
Exports	[e]315	[e]313	[e]151	[e]265	[e]226	[e]157	[e]894	[e]3,513	[e]285	[e]2,302	NA
Demand	8,789	8,908	9,050	8,810	6,810	6,647	6,425	7,060	7,396	16,043	10,729
U.S. DEMAND PATTERN											
Instruments	7,965	8,305	8,398	8,105	6,299	6,124	5,915	6,320	7,071	14,920	10,397
Other	824	603	652	705	511	523	510	740	325	1,123	332
Total U.S. demand	8,789	8,908	9,050	8,810	6,810	6,647	6,425	7,060	7,396	16,043	10,729

[e]Estimated. NA Not available. W Withheld to avoid disclosing company proprietary data.
[1]Excluding U.S. production.

STRUCTURE OF THE INDUSTRY

Because gallium is a byproduct metal and undergoes many refining and processing stages before a marketable product is produced, gallium is truly an international business. Most bauxite is mined in Australia, Africa, and South America, while gallium recovery and refining are currently centered in Europe. GaAs wafer and device fabrication is concentrated in the United States and Japan.

Many gallium producers have the facilities to recover 3N and 4N gallium and refine it to higher purity. Some gallium producers also have scrap recycling facilities. Table 8 shows current and projected capacities for each company that is involved in recovering, recycling, or purifying gallium metal, or has announced plans to construct new facilities. Virgin and recycle gallium plants produce 3N to 4N gallium, while purification plants yield gallium of 6N to 8N purity. Because of the nature of gallium processing, the only figures that should be considered when evaluating the long-term availability of gallium are the virgin gallium capacities.

GALLIUM RECOVERY, RECYCLE, AND PURIFICATION

Australia

Although gallium is not currently recovered in Australia, Rhône-Poulenc of France plans to construct a 50,000-kg/yr gallium extraction plant in Pinjarra, Western Australia, to be completed by the second half of 1988. The gallium source for the operation will be the Bayer liquors generated by Alcoa of Australia Ltd.'s alumina refinery at the same location, which uses locally mined bauxite as its feed source. When this plant is completed, it will be the largest gallium extraction plant in the world, producing 4N gallium metal.

Canada

Alcan Aluminium Ltd. completed a 10,000-kg/yr gallium recycling plant at Kingston, Ontario, in early 1986. GaAs scrap from both the United States and Canada is used as feed for the plant, to produce 4N gallium. Alcan also is constructing a new facility at its Jonquiere, Quebec, alumina refinery to produce virgin gallium, which is expected to be completed in 1988. The alumina plant uses bauxite from Brazil, Guinea, and Guyana as feed material. When the plant is completed, its capacity will be 4,000 kg/yr of 4N gallium metal.

Cominco recovers gallium at a 4,000-kg/yr refinery in Trail, British Columbia. Although the company also refines zinc concentrates at the same location, it does not recover gallium from these concentrates. Instead crude gallium metal, gallium oxide, scrap, and flue dust purchased from outside sources are used as plant feed to produce 6N to 7N gallium metal.

China

Gallium metal of 3N to 4N purity is recovered in Shangdong at the Nanding alumina plant. Bauxite is mined locally, and the gallium extraction plant has a capacity of 8,000 kg/yr. Most of the gallium produced in China is shipped to Japan for refining to 6N and 7N metal.

Czechoslovakia

Gallium metal is produced at the Ziar nad Hronom alumina refinery, which uses bauxite from Hungary and Yugoslavia as its raw material. At the 3,000-kg/yr plant, 3N to 4N gallium metal is produced, and most of the

Table 8. - World gallium plant capacities[e]

Plant location	Ownership	Yearend capacity, mt 1987	1988	1989	1990
Primary (virgin) gallium extraction plants:					
Australia	Rhône-Poulenc S.A.	0	50	50	50
Canada	Alcan Aluminium Ltd.	0	4	4	4
China	Shangdong Aluminium Co.	8	8	8	8
Czechoslovakia	Czechoslovakian Government	3	3	3	4
France	Rhône-Poulenc S.A.	20	20	20	20
Germany, Federal Republic of	Ingal International Gallium GmbH	12	12	15	20
Hungary	Hungarian Aluminium Co.	4	4	8	8
India	Madras Aluminium Co.	([1])	([1])	([1])	3
Japan	Dowa Mining Co.	7	7	7	7
Do	Sumitomo Chemical Co. Ltd.	10	10	10	10
Norway	Elkem A/S	5	5	5	5
United States	Eagle-Picher Industries Inc.	3	3	3	3
Do	Musto Explorations Ltd.	9	9	9	9
Do	Sulzer Brothers Inc.	0	15	15	15
Total		81	150	157	166
Secondary gallium recovery plants:					
Canada	Alcan Aluminium Ltd.	10	10	10	10
Do	Cominco Ltd.	0	0	0	4
France	Société Minière et Metallurgique de Peñarroya	([1])	([1])	10	10
Germany, Federal Republic of	Ingal International Gallium GmbH	6	6	6	6
Do	Preussag AG Metall	8	8	8	8
Japan	Dowa Mining Co.	2	2	2	2
Do	Rasa Industries Ltd.	3	3	3	3
Do	Sumitomo Chemical Co. Ltd.	5	5	5	5
Do	Sumitomo Metal Mining Co. Ltd.	3	3	3	3
Do	Ote Metal Co.	6	6	6	6
United Kingdom	Mining and Chemical Products Ltd.	3	3	3	3
United States	Recapture Metals Inc.	4	4	4	4
Total		50	50	60	64
Gallium purification plants:					
Canada	Alcan Aluminium Ltd.	0	0	5	5
Do	Comino Ltd.	4	4	4	4
France	Rhône-Poulenc S.A.	20	20	20	20
Germany, Federal Republic of	Ingal International Gallium GmbH	15	20	20	20
Japan	Dowa Mining Co.	7	7	7	7
Do	Sumitomo Chemical Co. Ltd.	10	10	10	10
Switzerland	Alcan Aluminium Ltd.	10	10	10	10
United Kingdom	Mining and Chemical Products Ltd.	3	3	3	3
United States	Eagle-Picher Industries Inc.	7	7	7	7
Do	Rhône-Poulenc S.A.	0	50	50	50
Total		76	131	136	136

[e]Estimated. [1]Less than 1/2 unit.

gallium is exported to Japan for purification. Czechoslovakia plans to expand this plant's capacity to 4,000 kg/yr by 1990.

France

Rhône-Poulenc operates the world's largest gallium extraction plant at Salindres, with a capacity of 20,000 kg of gallium per year. Bayer liquor from Pechiney's Gardanne alumina refinery, which recovers alumina from bauxite mined locally and in Guinea, is used as feed for the gallium extraction plant. Rhône-Poulenc produces 4N gallium, which is then further refined to 6N and 7N gallium at Salindres. The bulk of this high-purity gallium is shipped to the United States and Japan.

Société Minière et Metallurgique de Peñarroya S.A. plans to increase its capacity for recycling GaAs scrap to 10,000 kg/yr by 1989. Peñarroya already has a small capability to recover gallium from scrap at its plant at Noyelles-Godault.

Federal Republic of Germany

Ingal International Gallium GmbH operates two gallium recovery plants at Schwandorf and Lunen with a combined extraction capacity of 12,000 kg/yr. VAW's two alumina plants at the same locations, which recover alumina from bauxite mined in Australia and Guinea, supply Bayer liquor to Ingal's gallium extraction circuit. VAW's alumina refinery in Lunen is scheduled to close in 1988, but Ingal plans to construct a new 20,000-kg/yr plant in grade as a replacement, which is expected to be fully operational by mid-1989. In addition to extracting virgin gallium, Ingal also purifies its gallium to 6N to 7N purity at Schwandorf and recovers gallium from GaAs scrap.

Most of the high-purity gallium is exported to the United States and Japan.

Preussag AG Metall operates an 8,000-kg/yr gallium recycling facility in Langelsheim to recover 3N to 4N gallium from GaAs scrap.

Hungary

Virgin gallium is extracted at Hungarian Aluminium Corp.'s facility in Ajka. Bayer liquor from the company's alumina refinery, which uses locally mined bauxite as its raw material, is used as the gallium source for the 4,000-kg/yr plant. Gallium of 3N to 4N purity is recovered in Hungary; most of it is shipped to Japan for refining. In 1986, Hungarian Aluminium announced that it planned to double the capacity of its plant by 1988.

India

Madras Aluminium Co. Ltd. began pilot-scale production of virgin gallium metal in late 1986 at its plant in Mettur, Tamil Nadu. The company's alumina refinery at the same location supplies the Bayer liquor feed stock, using locally mined bauxite as the alumina plant's raw material source.

Japan

Two companies in Japan, Dowa Mining and Sumitomo Chemical, produce virgin gallium, recover gallium from scrap, and produce 6N to 7N gallium metal for the Japanese market. Dowa Mining recovers gallium from zinc residues at its 7,000-kg/yr gallium extraction plant in Akita, Honshu. Zinc residues are generated at the Akita Zinc Co. Ltd. plant, which is 52 pct owned by Dowa Mining, from zinc ores mined at Akita Zinc's Uchinotai and Hanaoka Mines. Sumitomo Chemical recovers gallium at its 10,000-kg/yr plant in Niihama, Shikoku. Before the closure of its last operating alumina refinery in October 1986, Sumitomo Chemical used Bayer liquors from the alumina plant as its source of gallium. Both Dowa Mining and Sumitomo Chemical operate gallium purification facilities, where they produce 6N to 7N metal. In addition to refining their own productions, both companies purify imported 3N to 4N gallium, principally from China, Czechoslovakia, and Hungary.

Rasa Industries Ltd. operates plants at Miyako and Osaka that recover 3N to 4N gallium from GaAs scrap. Combined plant capacity is estimated to be 3,000 kg/yr. Two other companies began operating secondary gallium recovery facilities in 1987. Ote Metal Co., a subsidiary of Mitsubishi Metal Corp., began recovering 3N to 4N gallium from GaAs scrap at its 6,000-kg/yr plant at the Onahama refinery in January. Sumitomo Metal Mining Co. Ltd. began operating a 3,000-kg/yr secondary gallium recovery facility in Niihama in July.

Norway

Elkem began operating a newly constructed gallium extraction plant at its Bremanger ferroalloy plant site in July 1987. Aluminum smelter flue dusts from primary aluminum refineries in Mosjoen and Tyssedal, containing about 0.5 pct gallium, are used as the source material for the 5,000-kg/yr plant. Only small quantities of 3N to 4N gallium have been produced at this facility.

Spain

Early in 1988, Rhône-Poulenc announced that it had signed an agreement with the Spanish Government to purchase the entire output of gallium-containing residues from the Aluminia Espanola S.A. (Inespal) alumina refinery in San Ciprian. Although no date has been given for the start of construction, Rhône-Poulenc plans to construct a gallium extraction facility near San Ciprian. The residues are estimated to contain up to 30,000 kg/yr of gallium, but the plant capacity has not been stated.

Switzerland

Alcan operates a 10,000-kg/yr gallium purification plant in Rorschach, which it purchased from Swiss Aluminium Ltd. in 1985. The Rorschach plant produces gallium of 6N to 8N purity using 3N to 4N gallium recovered from scrap at the company's plant in Canada as the feed material. Most of Alcan's production is shipped to the United States, with a small quantity exported to Japan.

U.S.S.R.

Although no data are available to determine quantities and locations of plants that recover gallium, it is believed that the U.S.S.R. recovers, purifies, and consumes significant quantities of gallium for IC production. In 1986, it was announced that the U.S.S.R. plans to increase its production and usage of gallium, according to the 1986-90 5-year plan.

United Kingdom

Mining and Chemical Products Ltd. operates a 3,000-kg/yr gallium recycling facility in Alperton, Wembley, to recover gallium from GaAs scrap generated at its electronic materials division. In addition to recovering 3N to 4N gallium from scrap, the company has facilities to produce high-purity gallium for the U.S. and European markets.

United States

St. George Mining operates a mine and processing plant near St. George, UT, to recover gallium contained in iron oxide minerals that remained at an abandoned copper mine. Gallium metal of 5N purity was produced at the 9,000-kg/yr plant until September 1987, when the plant was temporarily closed for repairs. In mid-1988, St. George Mining field for bankruptcy. Much of the gallium to be produced was expected to be shipped to Eagle-Picher's plant in Quapaw, OK, for refining to 6N to 7N purity. Eagle-Picher has a 3,000-kg/yr capacity to recover gallium from zinc residues generated at its Quapaw plant, but has not produced virgin gallium since 1982. However, the company does produce 4N, 5N, and 7N gallium metal from gallium concentrates and GaAs and GaP scrap.

Sulzer Brothers Inc. plans to complete construction of a 15,000-kg/yr gallium extraction facility by the end of 1988. The plant, in Gramercy, LA, will obtain Bayer liquor from Kaiser Aluminum & Chemical Corp.'s alumina refinery at the same location, which uses bauxite from Jamaica as its feed source. The first 2 years' production is scheduled to be shipped to Europe in the form of a gallium chloride solution to be used in a solar neutrino capture experiment. After this commitment has been fulfilled, a decision will be made concerning the plant's future gallium production.

Rhône-Poulenc plans to construct a 50,000-kg/yr gallium purification plant at Freeport, TX, by 1988. The plant is expected to use the 3N to 4N gallium recovered at the company's plant in Australia as feedstock. The 6N to 7N gallium metal produced at the refinery is expected to be used by the United States.

Recapture Metals Inc. began operating a 4,000-kg/yr gallium recycling facility in Blanding, UT, in 1986. Although the company can produce gallium with a purity of 6N to 7N, most of its product is 3N to 4N gallium.

HIGH-PURITY ARSENIC PRODUCTION

Arsenic is recovered as arsenic trioxide in about 20 countries from the smelting or roasting of nonferrous metal ores or concentrates. Arsenic metal, which accounts for only about 3 pct of the world demand for arsenic, is produced by the reduction of arsenic trioxide. Commercial-grade arsenic metal, 99-pct-pure arsenic, is produced in only a few countries, and this grade accounts for the majority of arsenic metal production. High-purity arsenic, 4N purity or greater, for use in the semiconductor industry is produced by about 10 companies. Furukawa Co. Ltd. in Japan and Preussag in the Federal Republic of Germany are believed to be the world's largest producers, with reported capacities of 30,000 kg/yr and 15,000 kg/yr, respectively. Other high-purity arsenic producers include Cominco in Canada, Mitsubishi Metal and Rasa Industries in Japan, and Johnson Matthey Ltd. and MCP Electronic Materials Ltd. in the United Kingdom.

GALLIUM ARSENIDE INGOT, WAFER, AND DEVICE MANUFACTURERS

Table 9 lists companies involved in various phases of GaAs wafer and device manufacture. As is evident from the number of companies listed for these countries, most of the advanced GaAs manufacturing occurs in the United States and Japan. Some companies are fully integrated from GaAs ingot manufacture through device manufacture, while others make either wafers or devices.

Table 9. - Gallium arsenide ingot, wafer, and device manufacturers

Country and company	Ingot and wafer manufacture		Epitaxy				Device manufacture		
	LEC	HB	LPE	VPE	MOCVD	MBE	Optoelectronic	Analog	Digital
Canada: Cominco Electronic Materials Ltd.	x								
France:									
Picogiga						x			
The Philips Group				x					
Thomson CSF					x	x			
Germany, Federal Republic of:									
Siemens AG	x			x	x	x			
Wacker Chemitronic AG	x	x							

Table 9. - Gallium arsenide ingot, wafer, and device manufacturers—Continued

Country and company	Ingot and wafer manufacture		Epitaxy				Device manufacture		
	LEC	HB	LPE	VPE	MOCVD	MBE	Optoelectronic	Analog	Digital
Japan:									
Dowa Mining Co.	x								
Fujitsu Ltd.							x	x	
Furukawa Co. Ltd.	x								
Hitatchi Cable Ltd.	x	x	x	x					
Hitatchi Manufacturing Co. Ltd.							x	x	
Iwaki Co. Ltd.	x								
Japan Victor Corp.							x		
Matsushita Electric Corp.							x	x	
Mitsubishi Electric Corp.						x		x	
Mitsubishi Metal Corp.	x	x		x					
Mitsubishi Monsanto Chemical Co. Ltd.	x	x	x	x					
NEC Corp.							x	x	
Nippon Mining Co. Ltd.	x								
Oki Electric Industry Co. Ltd.							x		
Sanyo Electric Co. Ltd.							x		
Sharp Corp.							x		
Shin-Etsu Semiconductor Corp.	x								
Showa Denko K.K.	x								
Stanley Electric Co. Ltd.							x		
Sumitomo Electric Industries Ltd.	x	x	x	x					
Sumitomo Metal Mining Co. Ltd.	x	x							
Toshiba Corp.	x						x		
Sweden: Semitronics AB	x								
United Kingdom:									
General Electric Co. (U.K.)				x		x	x	x	x
ICI Wafer Technology	x								
MCP Electronic Materials Ltd.		x							
Plessey PLC					x			x	x
United States:									
Airtron Div. of Litton Industries	x								
Anadigics Inc.					x			x	x
Applied Solar Energy Corp.					x		x		
AT&T Bell Laboratories					x	x	x		x
Bertram Laboratories	x								
Crystal Specialties Inc.		x	x	x	x				
Epitronics Corp.			x		x				
Ford Microelectronics Div. of Ford Motor Co.					x				x
General Electric Co.					x	x	x	x	
General Instrument Corp.				x			x		
GigaBit Logic Inc.								x	x
Harris Microwave Semiconductor Corp.	x							x	x
Hewlett Packard Inc.	x	x	x	x			x	x	
Honeywell Inc.					x	x	x		x
Hughes Aircraft Co.	x						x	x	x
IBM Corp.								x	x
ITT Corp.					x		x	x	x
Kopin Corp.					x		x		
Laser Diode Inc.		x					x	x	
M/A-Com Inc.		x							
McDonnell Douglas Corp.									x
Morgan Semiconductor Div. of Ethyl Corp.	x	x			x				
Motorola Inc.							x	x	
Pacific Monolithics Inc.								x	x
Rockwell International Corp.	x				x	x		x	x
Siemens Corp.			x				x		
Spectrum Technology Corp.	x								
Spire Corp.					x		x		
Texas Instruments Inc.	x						x	x	x
TriQuint Semiconductor Inc.								x	x
TRW Inc.			x			x	x	x	
Varo Inc.					x		x		
Vitesse Semiconductor Corp.									x
Westinghouse Electric Co.	x			x	x			x	

RESEARCH AND DEVELOPMENT

Considerable research is being done concerning all phases of gallium extraction, GaAs material properties, and GaAs-based device manufacturing. Because GaAs IC manufacture is still in the developmental stage, much of the research activity centers on designing and manufacturing devices.

The Department of Defense sponsors a great deal of gallium research through the Defense Advanced Research Projects Agency (DARPA) and the National Aeronautics and Space Administration (NASA) as well as through the service branches' laboratories. Over the past few years, DARPA's focus in funding projects has been to increase the efficiency of processing GaAs devices. Although a variety of microwave and digital ICs have been fabricated from GaAs, many of these were prototype devices. Projects funded through DARPA were principally designed to increase the limited production of the prototype devices to full-scale manufacturing. Improving the manufacturing process may allow more complex ICs to be developed with increased radiation resistance and faster speed. By contrast, NASA is principally investigating optoelectronic devices, particularly solar cells. NASA's main thrust is to increase the energy efficiency and reduce the cost of GaAs-based solar cells.

In 1986, the Department of Defense announced that it would begin a $135 million program to develop MMICs for military electronic applications. The program, expected to begin in 1988, is called Mimic for Microwave/Millimeter Wave Monolithic Integrated Circuit. Mimic would provide funds for companies that are already involved in GaAs research to accelerate their activities.

Most of the companies that are involved in the commercial GaAs market, both in optoelectronic devices and ICs, are involved in the development of devices that optimize the properties of GaAs. Among the new devices that are being developed are the high-electron-mobility transistor (HEMT), heterojunction bipolar transistor (HBT), ballistic transistor, and quantum-well laser. HEMTs consist of an undoped GaAs substrate with a thin epitaxial layer of silicon-doped GaAlAs on top. When an electric current is passed through the HEMT, electrons from the impurity atoms in the GaAlAs layer fall into the GaAs layer, where they move very fast. HBTs operate in essentially the same manner, but the GaAlAs layer is more highly doped. Both HEMTs and HBTs could increase signal processing speed in MMICs and digital ICs. A ballistic transistor is basically a sandwich structure with two GaAlAs layers on both sides of an ultrathin GaAs layer. As in an HEMT device, electrons from the GaAlAs layer fall into the GaAs layer and pick up speed. But because the GaAs layer is so thin, electrons pass through the GaAs layer and into the second GaAlAs layer without slowing down. This enhanced electron movement could increase the speed of digital ICs and would allow MMICs to operate at high frequencies. The quantum-well laser is fabricated in the same way and with the same materials as the ballistic transistor, but instead of passing through the GaAs layer, electrons are trapped in this layer. By confining the charge carriers to this very small area, the chance is increased that they will recombine to emit light. Consequently, this structure increases the amount of light generated for a specific electrical signal (*6*). Development of these new devices has been made possible with the advent of MOCVD and MBE, which are capable of depositing ultrathin layers on a substrate.

With increased emphasis on developing new devices, demands have been placed on the GaAs substrate manufacturers to supply better quality and more uniform substrates. Consequently GaAs wafer manufacturers have been refining their crystal growth techniques to produce material with fewer defects, to improve the yield from gallium and arsenic metals to GaAs wafers, and to scale up production. At the same time, wafer manufacturers are trying to produce larger diameter wafers that ultimately could increase the yield from wafer to device.

Companies involved in epitaxial growth are also working to improve properties such as the uniformity in the thickness and composition of the epitaxial layers. Recently metal-organic molecular beam epitaxy (MOMBE), also referred to as chemical beam epitaxy, has been developed to combine the advantages of MOCVD and MBE. These advantages include superior epitaxial layer thickness and uniformity, defect-free surfaces, the ability to grow layers on more than one wafer at a time, and the ability to introduce and control phosphorus atoms for optoelectronic device fabrication. MOMBE was introduced in early 1987.

Work is also being done on combining GaAs with other materials to take advantage of the best qualities in each material. Prototypes of GaAs epitaxial layers grown on silicon substrates were recently produced, and sample quantities have been shipped to customers for testing. By using GaAs layers on a silicon wafer, the superior structural properties of silicon can be combined with the electrical and optical properties of GaAs. Larger, more durable wafers can be produced with light-emitting properties and increased radiation resistance. GaAs can be deposited by MOCVD or MBE over the entire silicon wafer, called blanket epitaxy, or islands of GaAs can be epitaxially deposited on the silicon wafer, called selective epitaxy. Wafers produced by blanket epitaxy could replace bulk GaAs wafers for GaAs MMICs and digital ICs. Wafers produced by selective epitaxy can combine silicon ICs with GaAs optoelectronic devices, GaAs MMICs, or GaAs digital ICs. Blanket epitaxial wafers would require less gallium than that consumed in the fabrication of bulk GaAs wafers, and selective epitaxial wafers would allow

GaAs to be used in areas in which its use is not currently feasible.

In solar cells, where GaAs has not supplanted silicon to any great degree, epitaxial deposition of GaAs layers on germanium substrates may represent a hybrid substitute material for silicon. GaAs is fragile and can only be deposited in thick layers on a GaAs substrate. This puts GaAs at a disadvantage in comparison with silicon, which is sturdy and can be epitaxially grown in thinner layers. Germanium substrates are stronger and less costly than GaAs substrates, and GaAs epitaxial layers can be grown thinner using MOCVD. Consequently the increased energy efficiency and radiation resistance of GaAs solar cells can be exploited, while reducing the total weight of GaAs-based solar cells. While providing the same power as silicon solar cells, GaAs-on-germanium solar cells can be made smaller, which allows a satellite to carry a larger payload.

By continuing to push the limits of GaAs technology, researchers have also developed the optical equivalent of the transistor, a GaAs-based IC that controls light in the same manner a transistor controls electrical current. Thousands of alternating layers of GaAs and GaAlAs, each 40 atoms thick, are used in the construction of the IC. When a voltage is applied, the material becomes transparent, allowing a laser beam to shine through. A second, less powerful laser beam concentrates the electrical voltage in certain layers, which become opaque. Thus the second laser beam controls the transmission of the first laser beam. The outgoing light beam from one device can then be used as an input for a second device. Development of these devices could be a step in developing an optical computing device that would use light to transmit information rather than using electrical power.

Basic research is being performed on the extraction of gallium from nontraditional source materials. The Bureau of Mines has investigated the extraction of gallium from phosphorus flue dust and low-grade domestic resources (*7-8*). Work is also being done by private firms to recover gallium from coal fly ash and phosphorus flue dust.

LEGISLATION AND GOVERNMENT PROGRAMS

Historically, gallium has not been impacted by legislative action, except for transportation requirements. In 1976, the U.S. Department of Transportation classified gallium as a hazardous material for purposes of transportation. The amendment to the regulations prohibits transportation of liquid gallium aboard aircraft and specifies requirements for packaging solid gallium for aircraft transport and solid and liquid gallium for surface transport (*9*).

Tariff rates for gallium and gallium oxide are shown in table 10. Under the proposed United States-Canada Free Trade Agreement, tariffs for gallium metal traded between the two countries will be removed on January 1, 1993.

Table 10. - U.S. import duties for gallium, January 1, 1989

Item	Number	Most favored nation (MFN)	Non-MFN
Gallium oxide.	2825.90.5000	3.7 pct ad valorem	25.0 pct ad valorem.
Gallium metal	8112.91.0000	.. do	Do.

STRATEGIC FACTORS

Despite the fact that gallium is currently being used in some sophisticated military and satellite systems and is planned to be incorporated into additional systems, it has not been designated as a material to be added to the National Defense Stockpile. In 1986, Government and private agencies assessed the need to stockpile gallium, but because construction of additional gallium extraction plants is planned in North America, it was determined that in the event of a national emergency, gallium supplies would be adequate. If consumption increases dramatically over the next few years, it is likely that this assessment would be reevaluated.

Although import dependence for gallium cannot be calculated according to the Bureau's formula, by comparing the U.S. production to the U.S. demand, it is apparent that the United States is highly dependent on imports to meet its needs. This import dependence is likely to continue because there is no planned construction of gallium extraction plants in the United States that would increase the commercial supply. Musto Explorations' existing extraction plant in Utah was operating at a significantly reduced capacity before its closure, and the gallium output of Sulzer Brothers plant under construction in Gramercy, LA, will be shipped to Europe for at least 2 years.

With the rapid technological progress, especially in GaAs IC development, the status of world supply and demand is changing dramatically. GaAs has advanced from a laboratory curiosity, a decade or so ago, to a material with distinct applications and almost no effective substitutes at present. Development of fiber optic telecommunications systems, the advent of sophisticated electronic military warfare, the widespread use of consumer electronics, and the need to process vast quantities of data in the shortest time possible have provided the impetus for implementing the large number

of GaAs research and development programs. By continuing to push the limits of GaAs technology, its applications have expanded. At the same time, continuing research into developing other "high-tech" materials, such as InP, superconductors, and organic polymer semiconductors, may yield materials with properties superior to those of GaAs. Development of these potential substitutes could radically alter the future of GaAs.

REFERENCES

1. Zwiebel, K. Photovoltaic Cells. Chem. and Eng. News, v. 64, No. 27, July 7, 1986, pp. 34-48
2. Katrak, F. E., and J. C. Agarwal. Gallium: Long-Run Supply. J. Met., v. 33, No. 9, Sept. 1981, pp. 33-36.
3. Beja, M. Method of Extracting Gallium Oxide From Aluminous Substances. U.S. Pat. 2,574,008, Nov. 6, 1951.
4. de la Breteque, P. Method of Recovering Gallium From an Alkali Aluminate Lye. U.S. Pat. 2,793,179, May 21, 1957.
5. Frensley, W. R. Gallium Arsenide Transistors. Sci. Am., v. 257, No. 2, Aug. 1987, pp. 80-87.
6. Brody, H. Ultrafast Chips at the Gate. High Technol., v. 6, No. 3, Mar. 1986, pp. 28-35.
7. Judd, J. C., M. P. Wardell, and C. F. Davidson. Extraction of Gallium and Germanium From Domestic Resources. Paper in Light Metals 1988. Metall. Soc. AIME, 1987, pp. 857-862.
8. Neylan, D. L., C. P. Walters, and B. W. Haynes. Gallium Extraction From Phosphorus Flue Dust by a Sodium Carbonate Fusion-Water Leach Process. Paper in Recycle and Recovery of Secondary Metals. Metall. Soc. AIME, 1986, pp. 727-733.
9. Federal Register. V. 41, No. 172, Sept. 2, 1976, pp. 37114-37115.

OTHER SOURCES

U.S. Bureau of Mines publications:

Gallium. Ch. in Mineral Commodity Summaries, annual.

Gallium. Ch. in Minerals Yearbook, annual.

Gallium. Ch. in Mineral Facts and Problems, quinquennial.

☆ U.S. GOVERNMENT PRINTING OFFICE: 611-012/00,024

INT.-BU.OF MINES,PGH.,PA. 28830