GERMANIUM AND GERMANIUM COMPOUNDS

1. Introduction

Germanium (Ge) was discovered in 1886 by the German scientist Clemens Winkler (1); however, no uses were established over the first half of its known existence. It has an atomic number of 32, falling in Group IV of the periodic table of the elements just below silicon (Si).

Eagle-Picher separated Ge from their zinc and lead mine production in the Tri-State District (New York–New Jersey–Connecticut) in about 1930 as a necessity, as the presence of Ge hindered the electroplating of zinc in metallurgical processes, particularly the emerging automobile industry. In the early 1930s, E-P and Otavi Minen were first in commercial production, although the "market" was very small at the time, limited to university and government laboratories. During World War II, point-contact diode action was noted in grains of Ge. Production accelerated during World War II, as Ge was used in the first radar devices developed in the United Kingdom, then moved to the United States.

The semiconductor properties of Ge offered a new field of research opportunities, and led to the development of the first transistor by Bell Laboratories. The usage of Ge in power transistors and telephonic applications fueled Ge's strong growth to usage exceeding 100 tons annually during the 1950s and 1960s. During the latter part of this period, the abundance and processing ease of silicon have allowed Si to fuel the semiconductor, telecommunications, and computer age through the 1990s. However, germanium is still important today in these and many more industries.

2. Sources and Supplies

The current producers of germanium are Tech Cominco (Canada), Eagle-Picher (United States), Umicore (Belgium), PPM-Metaleurop (Germany), SE Germanium (Russia), ZTM (Ukraine), Chilong Zinc and Germanium Inc. (China), JEMCO (Japan), Zinc Ox Resources (Namibia), and the Blue Nill Mine (Kinshasa, Congo).

Germanium is sourced primarily as by-product; however, when the price was near the $2000/kg mark during the 1996 calendar year, it became economically feasible to recover Ge from several sources for the Ge alone. In particular, these sources were the Apex mine (Utah, USA), Sakhalin coal (Russia), copper residue (Chile), zinc residue (Tennessee, USA), oil shale (Canada), and others. Since the price has subsequently fallen to half the value of 1996, recovery efforts from these sources has been discontinued. Their availability and the continued engineering efforts to lower costs of recovery and processing may indeed establish a long-term price ceiling should demand surge be sustained for several years.

Government stockpile sales were factors in the price movements during the late 1990s (2). During the Strategic Stockpile buildup of the 1980s, substantial quantities were accumulated in the United States and the (then) Soviet

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Union. The United States' goal under the Reagan Administration was 146 tons of germanium. After the Persian Gulf War and breakup of the USSR into the Commonwealth of Independent States (CIS), later to be known as Former Soviet Union (FSU), the legislatures of all countries reduced defense spending significantly. The last U.S. stockpile orders were shipped during 1991, making a total of over 68 tons quantity. USSR totals were never fully disclosed, but totaling what has been sold and exported subsequently would indicate that about 80 tons Ge content in the form of metal bars and dioxide was held in 1991 in the Ukraine and Russia.

The FSU germanium was exported in two surges: (1) 1993/94, which was also a period of Ge low demand and the additional material added to the supply abundance pushing prices down to record low levels, and (2) 1997/98, which was just past the peak of record high prices. There are no known remaining government-held Ge stocks in the FSU. The U.S. Defense Logistics Agency sold a small quantity in 1993, leaving a balance of 68 tons. Congress authorized the disposal of 40,000 kg to begin in fiscal year 1996 (October 1, 1995 to September 30, 1996). This was during the height of the demand and price peak period, and if material had actually been sold, the price levels may have been moderated. However, the money realized through the sale of the newly authorized stockpile materials (which included other metals besides Ge) was earmarked for a particular purpose, which proved unpopular with the administration, and the enabling legislation did not become law. In fiscal year 1997, 6 tons was approved for sale on a sealed bid basis, but only 4566 kg were sold as the demand had been met and supply was in surplus. Beginning in fiscal year 1998, a maximum of 8 tons were to be sold yearly. Stockpile status as of March 31, 2003 was about 42 tons (3).

3. Properties

The physical, thermal, and electronic properties of germanium metal are shown in Table 1. Optical properties are given in Table 2.

4. Chemical Properties

4.1. Germanium Metal.

Germanium is quite stable in air up to 400°C where slow oxidation begins. Oxidation becomes noticeably more rapid above 600°C. The metal resists concentrated hydrochloric acid, concentrated hydrofluoric acid, and concentrated sodium hydroxide solutions, even at their boiling points. It is not attacked by cold sulfuric acid but does react slowly with hot sulfuric acid. Nitric acid attacks germanium at all temperatures more readily than does sulfuric acid. Germanium reacts readily with mixtures of nitric and hydrofluoric acids and with molten alkalies and more slowly with aqua regia. The principal reaction route for the mixed acids is the oxidation of the germanium by one constituent, then dissolution of the oxide by the other constituent. The reaction with fused alkalies is a direct oxidation with the release of hydrogen.

Table 1. **Properties of Germanium**

Parameter	Value
Physical properties	
atomic weight	72.59
density at 25°C, g/cm^3	5.323
atomic density at 25°C, at/cm^3	4.416×10^{22}
lattice constant at 25°C, a_o, nm	0.565754
surface tension, liquid at mp, mN/m(=dyn/cm)	650
modulus of rupture, MPa[a]	110
Mohs' hardness	6.3
Poisson's ratio at 125–375 K isotopes	0.278
mass number	70 72 73 74 76
natural abundance, %	20.4 27.4 7.8 36.6 7.8
Thermal properties	
melting point, °C	937.4
boiling point, °C	2830
heat capacity at 25°C, J/(kg · K)[b]	322
latent heat of fusion, J/g[b]	466.5
latent heat of vaporization, J/g[b]	4602
heat of combustion, J/g[b]	7380
heat of formation, J/g[b]	4006
vapor pressure, kPa[c]	
at 2080°C	1.33
at 2440°C	13.3
at 2710°C	53.3
at 2830°C	101.3
coefficient of linear expansion, 10^{-6}/K	
at 100 K	2.3
at 200 K	5.0
at 300 K	6.0
thermal conductivity, W/(m · K)	
at 100 K	232
at 200 K	96.8
at 300 K	59.9
at 400 K	43.2
Electronic properties	
intrinsic resistivity at 25°C, Ω · cm	53
intrinsic conductivity type	N (negative)
intrinsic drift mobility at 25°C, $cm^2/(V \cdot s)$	
electron	3800
hole	1850
band gap, direct, minimum eV	
at 25°C	0.67
at 0 K	0.744
number of intrinsic electrons at 25°C, cm^{-3}	2.12×10^{13}

[a] To convert MPa to psi, multiply by 145.
[b] To convert J to cal, divide by 4.184.
[c] To convert kPa to mm Hg, multiply by 7.5.

In compounds, germanium can have a valence of either 2 or 4. Although the divalent compounds tend to be less stable than the tetravalent ones, most can be stored at room temperature for years with no change in composition. At higher temperatures, most of the divalent compounds decompose. The syntheses and

Table 2. **Optical Properties of Germanium**

Wavelength, μm	Refractive index at 25°C	Absorption coefficient, cm^{-1}
1.8	4.134	7.0
1.9	4.120	0.68
2.0	4.108	0.010
4.0	4.0255	0.0047
6.0	4.0122	0.0068
8.0	4.0074	0.0150
10.0	4.0052	0.0215
10.6	4.0048	0.0270
11.0	4.0045	0.0295
11.9	4.0040	0.200
12.0	4.0039	0.170

properties of many germanium compounds have been reviewed (4) and properties of germanium bonds discussed (5). There is also an excellent earlier review of inorganic germanium compounds (6).

4.2. Germanium Tetrachloride.

Germanium tetrachloride [10038-98-8], $GeCl_4$, is made by the reaction of hydrochloric acid on germanium concentrates containing oxides or germanates. It can also be made by the reaction of chlorine on heated metallic germanium. The properties of $GeCl_4$ are shown in Table 3.

$GeCl_4$ is soluble in solvents such as acetone, absolute ethanol, benzene, carbon disulfide, carbon tetrachloride, chloroform, and diethyl ether. It is only slightly soluble in concentrated hydrochloric acid and the solubility drops with acid normality, reaching a minimum at 5 *N*. At HCl concentrations below 5 *N*, the tetrachloride begins to hydrolyze to GeO_2. Germanium tetrachloride

Table 3. **Properties of Germanium Tetrachloride**

Property	Value
molecular weight	214.40
color	colorless
density at 25°C, g/cm^3	1.874
melting point, °C	−49.5
boiling point, °C	83.1
refractive index at 25°C, 0.5893 μm	1.464
heat capacity, C_p, of vapor at 25°C, $J/(kg \cdot K)^a$	449
heat of vaporization at bp, J/g^a	137
heat of formation at 25°C, J/g^a	−3318
vapor pressure, Pa^b	
at 225 K	10^2
at 253 K	10^3
at 294 K	10^4
at 356 K	10^5
at 462 K	10^6
at $T_c = 550K$	3.850×10^6

[a] To convert J to cal, divide by 4.184.

[b] To convert Pa to mm Hg, divide by 133.3.

is insoluble in concentrated sulfuric acid and does not react with it. The solubility of free chlorine in $GeCl_4$ can reach as high as 4 wt%, especially at low temperatures.

4.3. Germanium Tetrabromide and Germanium Tetraiodide.

Germanium tetrabromide [13450-02-5], $GeBr_4$, and germanium tetraiodide [13450-95-8], GeI_4, can be prepared easily by the reaction of the respective halogen and germanium metal or by the reaction of GeO_2 with HBr and HI solutions, respectively.

4.4. Germanium Fluoride.

Germanium Difluoride. Germanium difluoride[13940-63-1] is a white solid, mp 110°C, and $d_{23} = 3.7$ g/cm^3. This compound can be vacuum distilled. In a mass spectrometer, ions corresponding to $(GeF_2)_n^+$, where $n = 1 - 4$ have been observed at 361–403 K (7). At higher temperatures, GeF_2 disproportionates to GeF_4 (g), Ge (s), and GeF (g). Presumably the GeF [39717-71-0] formed is unstable and subsequently condenses and disproportionates. The initially reported (8) orange-red solid becomes red-brown going finally to the black of metallic Ge. The difluoride deliquesces (8) in moist air producing germanium(II) hydroxide. The difluoride is soluble in aqueous hydrofluoric acid and gives a solution having the reducing properties expected of divalent germanium. GeF_2 reacts with aqueous solutions of alkali metal fluorides to produce trifluorogermanites (9); eg, cesium trifluorogermanite [72121-41-6], $CsGeF_3$, and potassium trifluorogermanite [7212142-7], $KGeF_3$. The GeF^-;$_3$ ion is oxidized to GeF either by oxygen in neutral solution or by its reduction of H^+ to hydrogen in hydrofluoric acid solution. Germanium difluoride is soluble in ethanol (8), forms a reversible complex with diethyl ether (8), and forms a dimethyl sulfoxide complex [72121-40-5], $GeF_2 \cdot OS(CH_3)_2$, which is decomposed at 240°C (9).

Germanium difluoride can be prepared by reduction (8,10) of GeF_4 by metallic germanium, by reaction (7) of stoichiometric amounts of Ge and HF in a sealed vessel at 225°C, by Ge powder and HgF_2 (11), and by GeS and PbF_2 (12). GeF_2 has been used in plasma chemical vapor deposition of amorphous film (see PLASMA TECHNOLOGY; THIN FILMS) (13).

Germanium Tetrafluoride. Germanium tetrafluoride [7783-58-6] is a gas having a garlic-like odor, a reported (14) triple point of −15°C and 404.1 kPa (4.0 atm), and a vapor pressure near 100 kPa (ca 1 atm) at −36.5°C.Germanium tetrafluoride fumes strongly in air and is hydrolyzed in solution to form GeF^{2-};$_6$ ions. Germanium tetrafluoride can be prepared (14,15) by thermal decomposition of barium hexafluorogermanate [60897-63-4], $BaGeF_6$. Direct fluorination of germanium has been reported to give GeF_4 of higher purity (8). High purity GeF_4 is also manufactured by reaction of a finely powdered GeO_2 suspension in H_2SO_4 with UF_6 (16) or by the reaction of Ge metal or its oxide with F_2 or NF_3 (17). COF_2 has been used as a mild fluorinating agent to produce GeF_4 from GeO_2 (18). GeF_4 is used in ion implantation (qv) in semiconductor chips (see SEMICONDUCTORS)(19,20). Germanium tetrafluoride acts as a Lewis acid (21,22) to form complexes with many donor molecules. The tetrafluoride is commercially available.

Fluorogermanates. Fluorogermanic acid [16950-43-9] solutions, H_2GeF_6, are prepared by reaction of germanium dioxide andhydrofluoric acid or by hydrolysis ofgermanium tetrafluoride. Addition ofpotassium fluoride, barium

Table 4. **Properties of Germanium Dioxide**

	Form		
Property	Soluble	Insoluble	Vitreous
structure	hexagonal	tetragonal	amorphous
density at 25°C, g/cm^3	4.228	6.239	3.637
melting point, °C	1116	1086	
solubility in water, g/L soln			
at 25°C	4.53	insoluble	5.18
at 100°C	13	insoluble	
solubility in HCl, HF, NaOH solutions	soluble	insoluble	soluble

chloride(15), or other salts results in hexafluorogermanates such as potassium hexafluorogermanate [7783-73-5], K_2GeF_6, or $BaGeF_6$, both of which are stable at temperatures up to 500°C where $BaGeF_6$ starts to decompose to GeF_4 and BaF_2.

4.5. Germanium Oxides. Germanium dioxide [1310-53-8], GeO_2, is usually made by the hydrolysis of $GeCl_4$. GeO_2, also made by the ignition of germanium disulfide, exists in soluble, insoluble, and vitreous forms. The properties of these three forms are given in Table 4. The soluble form is the usual product of $GeCl_4$ hydrolysis. The insoluble form can be prepared by heating soluble oxide at 300–900°C, especially in the presence of about 0.5 wt% alkali halides. The glassy, or vitreous, form is prepared by melting either of the other forms and then cooling the melt.

Germanium monoxide [20619-16-3], GeO, can best be prepared in pure form by heating a mixture of Ge and GeO_2, in the absence of oxygen. At temperatures above 710°C, GeO sublimes from the mixture and condenses as a glassy deposit in the cooler part of the reaction vessel. Germanium monoxide is stable at room temperature.

4.6. Germanates. Germanates are usually prepared by the fusion of GeO_2 with alkali oxides or carbonates in platinum crucibles. Sodium heptagermanate [12195-31-2], $Na_3HGe_7O_{16} \cdot 4H_2O$, is precipitated by the neutralization of a sodium hydroxide solution of GeO_2 with hydrochloric acid to a pH above 7.

4.7. Germanides. Germanides can be formed by melting other metals with germanium in the proper stoichiometric concentrations and then freezing the melt. These compounds can also be prepared by vacuum-sintering the two metals together, usually followed by long annealing. Other procedures include the thermal dissociation of one germanide into another and the electrolysis of fused mixed salts. The preparation and properties of about 200 germanides have been tabulated and reviewed (23). One of the germanides that has been prepared most often is magnesium germanide [1310-52-7], Mg_2Ge.

4.8. Germanes. Germanium hydrides can be prepared by the reaction of a germanide, such as Mg_2Ge, with hydrochloric acid. Germane [7782-65-2], GeH_4, can also be produced by the reduction of $GeCl_4$ using lithium aluminum hydride or by the reduction of GeO_2 by sodium borohydride in water solution. The preparation and properties of the germanes have been reviewed (24,25).

4.9. Miscellaneous Inorganic Compounds. Germanium nitride [12065-36-0], Ge_3N_4, is about as inert as tetragonal GeO_2. It is prepared most easily from germanium powder and ammonia at 700–850°C. The nitride does not react with most mineral acids, aqua regia, or caustic solutions, even when hot. Germanium disulfide [12025-34-2], GeS_2, is an unusual and useful compound because it is insoluble in strong acids such as 6 *N* HCl and 12 *N* H_2SO_4. This insolubility permits the recovery of germanium from acid solutions by gassing with H_2S. The disulfide can also be made by the reaction of GeO_2 with sulfur.

4.10. Organogermanium Compounds. The field of organogermanium chemistry has drawn widespread interest for many years. Organogermanium compounds are generally characterized as having low chemical reactivity and relatively high thermal stability. Many syntheses begin with a Grignard reaction (qv). Many excellent reviews of the organogermanium literature have been published (26–38). Several organogermanium compounds have been produced in commercial quantities. These include spirogermanium [41992-22-7] (2-aza-8-germaspiro-[4,5]-decane-2-propanamine-8,8-diethyl-*N,N*-dimethyl dihydrochloride), $C_{17}H_{36}GeN_2 \cdot 2HCl$, and carboxyethyl germanium sesquioxide [27031-31-8] (3,3′-germanoic anhydride dipropanoic acid), $C_6H_{10}Ge_2O_7$. These compounds have been studied extensively for possible anticancer and blood pressure effects (39) (see CARDIOVASCULAR AGENTS; CHEMOTHERAPEUTICS, ANTICANCER).

4.11. Alloys. Many Ge alloys have been prepared and studied. Most have been made by melting Ge with another metal, much as germanides are made. Collections of binary phase diagrams and comments about many Ge alloys are available (40–43). An important new alloy, Argentium Sterling, has been patented which contains 1.2% Ge eliminating tarnish in sterling.

5. Manufacturing and Processing

5.1. Ore Processing. No mineral is mined solely for its germanium content. Almost all of the Ge recovered worldwide is a by-product of other metals, primarily zinc, copper, and lead (qv). The enriched copper–lead concentrates from Tsumeb, Namibia, have been treated in a vertical retort from which germanium sulfide is sublimed and separated (44). The copper–zinc ores of Katanga, Zaire, have been treated by roasting with H_2SO_4, followed by leaching and selective precipitation of the germanium with MgO (44). In the United States, zinc concentrates have been roasted and then sintered for zinc recovery (45). The sinter fume is chemically leached, and the germanium is selectively precipitated from the leach solution by fractional neutralization and sent to the germanium refinery. Because of the low solubility of germanium sulfide and tannate in acid solutions, germanium has been recovered by precipitating it from acid solutions using H_2S or tannic acid. Sulfide precipitates are usually oxidized using sodium chlorate or permanganate, followed by, or concurrent with, dissolution in concentrated HCl and distillation of the resulting $GeCl_4$. Tannic acid precipitates are usually upgraded by igniting the precipitate to the oxide and dissolving the oxide in concentrated HCl, with subsequent distillation of the $GeCl_4$. Germanium can also be recovered from the still residue in the distillation of zinc metal (46).

From 1986 to 1990, germanium was recovered intermittently from the Apex Mine near St. George, Utah. This was an unusual operation in that germanium was the principal product from the mine and gallium was a by-product. Copper was also recovered because the Apex Mine was an old abandoned copper mine. The process involved dissolution of the screened ore in sulfuric acid, followed by cementation of the copper, solvent extraction of the gallium, and precipitation of the germanium with H_2S. The GeS_2 precipitate was oxidized with sodium chlorate and dissolved in HCl. The $GeCl_4$ formed was distilled and then hydrolyzed to a crude GeO_2. The operation was not a financial success and the producer was forced into bankruptcy. The assets were purchased in 1989 by Hecla Mining Co., which made significant changes in the processing circuit, including the addition of a solvent extraction system for germanium recovery. However, even these changes were not enough to provide profitability to the operation in a declining market, and production was again stopped in August 1990.

In electrolytic zinc plants, which have become increasingly important for environmental reasons, germanium is precipitated, usually along with iron, during the purification of the $ZnSO_4$ electrolyte prior to electrolysis. Germanium is one of several impurities that have an adverse effect on zinc electrolysis. If the germanium concentration is high enough in the separated solids, economic recovery of germanium is possible. Several solvent extraction and ion-exchange (qv) processes have been developed (47–53) that provide better germanium separations, primarily from $ZnSO_4$ electrolytes.

5.2. Production. For assurance of the quality of product, strict protocols must be adhered to by the producer of the various Ge metal products and compounds. It is important that the producer be International Standards Organization (ISO) 9000-registered or certified.

The predominant process flow of germanium would follow this path: After the zinc ore is mined, crushed, separated, and concentrated, it is sent to a smelter where the zinc is recovered and the Ge becomes a part of the residue. This is typically $<1\%$ Ge content; however, certain zinc deposits can be "campaigned" where the material richer in Ge is run individually and the Ge percentage becomes enhanced in that residue to a few percent. This "Ge concentrate" is sent to a Ge producer who, using proprietary processes (ion exchange, solvent extraction, chlorination, distillation, and pyrometallurgy), formulates germanium tetrachloride. With sufficient purification, this is a salable product, but it is also an intermediary. A colorless liquid, $GeCl_4$ is classified as a corrosive liquid and is shipped in glass or stainless-steel containers, usually with overpacks.

5.3. Purification. A simplified flow diagram for a germanium refinery is shown in Figure 1. Regardless of the source of Ge, all Ge concentrates are purified by similar techniques. The ease with which concentrated germanium oxides and germanates react with concentrated hydrochloric acid and the convenient boiling point (83.1°C) of the resulting $GeCl_4$ make chlorination a standard refining step.

The $GeCl_4$ is hydrolyzed and dried as germanium dioxide, also both a product and intermediary. The GeO_2 is a white, granular powder, of density between 1.2 and 2.0 g/mL, and is then shipped in 5-kg-net-weight polyethylene bottles. Electronic-grade GeO_2 can be reduced under hydrogen at high temperatures to elemental Ge bars. This metal is then purified to 99.9999+% purity by passing multiple molten zones through the Ge bar segregating impurities to the nose and tail of the bar (which are removed and recycled to the $GeCl_4$ stage) (54). The silver/gray Ge bars are sheathed in polyethylene sleeves, wrapped, and

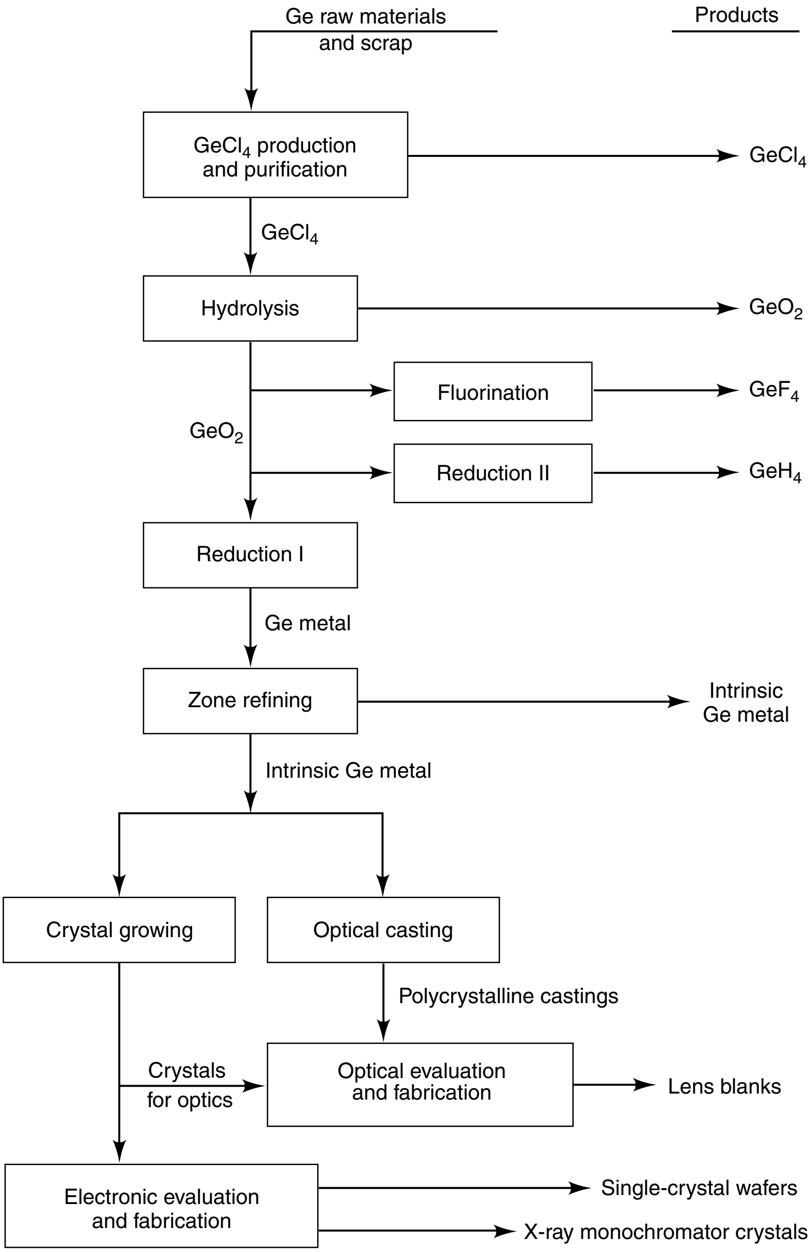

Fig. 1. Simplified germanium flow diagram.

boxed for protection against contamination and breakage during shipment. Ge metal is frangible, similar to glass.

Optical Ge is cast in large-grain, polycrystalline slabs or “grown” as poly- or monocrystalline using the *Czochralski process* (CZ), in which an orientated “seed” crystal is dipped into the melt and a single crystal is pulled at the solid–liquid interface. It is doped with an N-type impurity to fill smaller crosssectional electonic “holes” with “electrons,” to minimize infrared absorption. The Ge can also be doped to provide added high temperature performance or electromagnetic interference protection for the ir or infrared optical package. Windows and lenses are cut and ground using diamond-plated tools. Ingots are also grown by the Czochralski or vertical Bridgman process to produce monocrystalline wafers that become aerospace photovoltaic cell substrates suitable for GaAs layer deposition because of the close lattice match. The compound germane (GeH_4) is gaseous at room temperature and atmospheric pressure. It is produced under safety-monitored conditions and shipped usually in stainless-steel compressed-gas cylinders of up to 2-kg-net-weight contents. It must be shipped as a poison.

6. Economic Aspects

Because germanium is usually recovered as a by-product, its price and availability over the long term are subject to supply and demand considerations for its host products, such as zinc, in addition to the Ge value. This is not the case over the short term because producers, end users, and commodity brokers often have varying stocks of product and Ge-containing scrap. Therefore, short-term pricing is controlled mainly by demand.

This has been most evident during three periods in the last two decades. The period 1979–1981 found a 200% price increase due to sharply increased demands for Ge products from military infrared programs and optical fiber production. Ge producers were unable to meet the sharply higher demand during this period from regular sources, and lower-grade residues were utilized, incurring much higher processing costs and the resultant higher prices. At the end of 1981 the price for intrinsic Ge metal stood at $1060 per kilogram.

The next period for dramatic price change was 1992–1994. With the swift resolution of the Persian Gulf War in 1991 and the practically concurrent end of the Cold War, and subsequent breakup of the Soviet Union, came a significant reduction in demand for military equipment from all governments. During the same period, an economic recession was generally evident worldwide. Whereas the demand for Ge dropped dramatically with military cuts, the United States and the Soviet Union ceased purchasing for their strategic stockpiles. As Russia and the Ukraine came away from the Soviet Union as independent countries, they began to sell their considerable supplies of Ge and other materials to raise hard currency for modernization. These surplus supplies together with the reduction in demand caused prices to fall to as low as $400 per kilogram.

The third period of fluctuation saw a 400% increase from May 1995 to July 1996. This meteoric rise in the price to >$2000 per kilogram is generally attributed to Japanese PET [poly(ethylene terephthalate)] resin producers finding no longer seemingly unlimited availability, and with a strong yen:dollar ratio, importing over 43 tons of GeO_2, about 75% more than their annual usage. Because of the low demand and low prices during the previous four years, several producers had closed off some raw-material sources and could not ramp the remaining ones to meet this huge increase as the world’s economy began to recover and optical fiber demand and Ge solar cell substrates reached new peaks.

A balance of supply and demand was reached, particularly with the assurance of availability of U.S. stockpile materials from October 1996. Prices steadily dropped and U.S. stockpile Ge prices remained relatively stable between $800 and $1000 per kilogram over the period September 1997 through February 2000. In 2001, prices were lower, falling to $890/kg for the metal and $575/kg for the dioxide (3).

In 2002, world refinery production was estimated to be less than 50 t, a decrease of 30% from that of 2001. Recycling supplied 30 t of germanium worldwide, the same as 2001. The world total market supply was about 80 t in 2002, including only about 0.7 t released from the U.S. National Defense Stockpile.

Demand will remain weak with continued oversupply of both germanium and germanium oxide. Although the demand for germanium in 2001 for optical fiber has declined considerably, a recovery in the telecommunications sector in fiber optics for metropolitan and fiber-to-home consumption could mean a surge in demand for germanium. There is still growth in the infrared optics area, sterling alloys, and application in DVDs (3). The night vision system sector of the surveillance market is expected to grow from $\$560 \times 10^6$ to $\$750 \times 10^6$ by 2004 (55).

7. Grades and Specifications

Only germanium metal and germanium dioxide are commercially quoted and would be suitable for trading on a quasi-commodity basis. Other Ge compounds are custom-made to meet each end user or manufacturer's specification in regard to a particular impurity, packaging, or performance of the product. Even the metal and dioxide can vary significantly from a "standard" specification.

Germanium metal is "usually" understood to be intrinsic-grade, N-type, zone-refined, 99.9999+% purity, minimum. $40\ \Omega\cdot\psi\mu\ \alpha\tau\ <{}^{\circ}\mathrm{C}$ (equivalent to $50\ \Omega\cdot\psi\mu\ \alpha\tau\ \gtrless{}^{\circ}\mathrm{C}$). The U.S. Strategic Stockpile Specification is P-114-R. It requires a superior transmission range, because the purpose intended was infrared thermal imaging, in addition to the "usual" specifications. However, in many cases this required some dopant, making the metal only marginally useful when applied as crystal growth feed for γ-ray detectors.

Germanium dioxide is generally known in two grades: 99.99% purity (technical) and $\geq$99.9999+% purity (electronic). The 4N material is quoted in the biweekly publication *Metal Bulletin* and is also quoted by *Reuters* and other sources. The material is almost always of Chinese or FSU origin and the properties are subject to extreme variances from producer to producer and even between and within batches or lots. The Ge content has been seen to vary between 64 and 69%, with 0.4–5% moisture, volatile compounds, and sundry metallic and non-metallic impurities. Its value in commerce is simply that it is a "source" of germanium content. In contrast, the electronic grade is manufactured under strict conditions and is available from only a few sources.

8. Analytical Methods

The analysis of ores of germanium is usually done with an emission spectrograph but can be done in the field using the phenylfluorone method. Analysis of germanium refinery samples is usually done after fusion of the sample with KOH or

NaOH in nickel crucibles. Following distillation of the $GeCl_4$ from HCl solution of the fusion, the Ge can be determined gravimetrically, usually by precipitation of GeS_2 from acid solution and by ignition to GeO_2; titrimetrically, usually by reduction with sodium hypophosphite and titration with KIO_3 solution; or spectrally, using an atomic absorption spectrophotometer. The last procedure is not considered as accurate as either of the first two. Excellent reviews of the analytical chemistry of germanium have been published (56–58).

Analysis of refined germanium products is done in a wide variety of ways, including several methods that have become ASTM standards (58). Electronic-grade GeO_2 is analyzed using glow-discharge mass spectrograph to determine its spectrographic purity. Its volatile content is measured in accord with ASTM F5 and its bulk density with F6. Other ASTM standards cover the preparation of a metal billet from a sample of the oxide (F27), and the determination of the conductivity type (F42) and resistivity (F43) of the billet.

The type and resistivity of all grades of germanium metal are also measured in accord with F42 and F43. The transmission characteristics of optical-grade germanium are determined with an infrared spectrophotometer, and the measurement of the interstitial oxygen content of the metal is covered in F120 and F122. Germanium single crystals can be further evaluated in accord with ASTM F26, F28, F76, F389, F398, and F673.

The overall spectrographic purity of $GeCl_4$ can be determined by using an emission spectrograph to examine a sample of GeO_2 produced from the $GeCl_4$ by hydrolysis with deionized water. The trace metal impurities of concern to fiber optic producers are determined by flameless atomic absorption, and the hydrogen-bearing impurity concentrations are measured by infrared absorption of the $GeCl_4$. In certain electronics applications, a particular impurity in parts-per-billion (ppb) quantity may be totaly unacceptable.

9. Health and Safety Factors

The toxicity of germanium compounds is generally of low order. Usually, the toxicity or corrosive nature of the compound is by action of the other part of the compound than from the Ge content. Germane is considered a toxic gas. Users must employ calibrated detectors and adequate safety breathing apparatus and ventilation. Germanium tetrachloride is a corrosive liquid. Germanium tetrafluoride produces hydrogen fluoride in aqueous acidic solution. Users must consider it as similar in nature to silicon tetrachloride and hydrochloric acid, and provide protective clothing, face shields, gloves, and a neutralization chemical.

In many cases, production of by-products or waste from reactions or processes utilizing Ge compounds must be disposed of by licensed hazardous waste companies. Despite the “popularity” of ^{132}Ge as a health food or Oriental remedy, no producer advocates human or animal consumption of Ge products.

10. Recycling and Scrap Recovery

Except for the germanium metal and optical industries, which use a pure product that can be most easily recovered and recycled (eg, broken ir windows and lenses), other manufacturers’ processes [poly(ethylene terephthalate) and optical fiber production] and recycling effort were minimal until the 1995–1996 price spike. Now, recycling has become common practice, as several of the producers can recover Ge to below 1% content (depending on the matrix). In the case of optical fiber producers, the recoverable scrap occurs in the "baghouse" with a very light powder with which water has to be added to reduce volume, and in the "scrubber solution," which removes the vapors and maintains the internal pressure of the system. Broken BGO crystals and saw kerf have become valuable sources for recycling, as are spent ethylene glycol catalysts.

Given the finite nature of germanium, it is important that all processes be examined for all opportunities to recycle this valuable element.

11. Uses

Many of the uses of germanium and Ge compounds have been reviewed (46). Uses, by market, are listed in Table 5. Both U.S. and world use patterns have undergone drastic changes due to the strong downturn in the telecommunications industry (59). Germane (GeH_4) is used as a thin-film dopant in amorphous silicon (from silane) terrestrial solar cells and to make thin-film Si–Ge alloys for heterojunction bipolar transistors. The a-Si multispectral cells are flexible and inexpensive, and can be mass-produced. The major manufacturers are Solarex and United Solar Systems. Voltaix is the largest germane producer. The Si–Ge alloys being pioneered by IBM are heralded as being faster than silicon-based devices, yet less expensive than gallium arsenide–based devices. They can also be produced by evaporation of solid Si and Ge. Their initial mass usage is in HBTs for cellular phones.

The ^{132}Ge is also known as organic germanium, but formulated as bis-β carboxyethyl germanium sesquioxide, with formula weight 132. Although not approved for use by the U.S. Food and Drug Administration (FDA), over 5 tons is consumed as a health additive in the Far East. It is a white powder that can be encapsulated or pressed into a pill form. Studies have shown that although there is some health benefit indicated, there also are possible side effects.

Germanium tetrachloride is used in the largest application for Ge content, doping the core of optical fibers for telecommunications (60). The higher index of refraction of GeO_2 when blended with SiO_2 in the quartz fiber core continuously bends the lightwaves back toward the center, and transmissions of over 100 km can be obtained without signal boosting. The high bandwidth of the optical fiber make it superior to copper wire for carrying high volumes of data and graphics at high speed without electomagnetic interference. $GeCl_4$ is also used in the petroleum industry for catalyst formulation (47).

Table 5. **Germanium Usage (%) by Market, 2000**

optical fiber production	20
polymerization catalysts	35
infrared optics	25
electronic and solar applications	12
miscellaneous	8
Total	*100%*

Germanium dioxide finds uses in the phosphors industry, where the wavelength emission is superior for certain plant growth and other applications. GeO_2 has its major usage in the catalyst formulation for polymerization in poly(ethylene terephthalate), where more strength and heat resistance are needed in the bottles, as well as white polyester fibers that do not yellow with age. The GeO_2 is dissolved in ethylene glycol for application. The United States predominantly uses antimony trioxide as substitute, whereas the Japanese market and production methods rely on Ge- content for their bottles. The largest poly(ethylene terephthalate) (PET) producer in Japan is Mitsui. In another application for GeO_2, the hexagonal form is mixed with bismuth oxide and crystals of bismuth germanate are grown and used in the positron emission tomography detector.

Germanium metal is cast into various shapes and used as evaporation sources and sputtering targets for thin-film deposition. Ge metal is grown into crystals to be later fabricated into X-ray and neutron monochromaters, ultra-high-purity γ-ray detectors and bolometers. The crystals, when appropriately doped and formed into windows and lenses, are used in infrared thermal imaging for the military in target acquisition and search and track systems. This use also has commercial application in inspection of processes and products for heat dissipation and preventive maintenance (eg, electical transformers and railcar wheel and journal boxes).

Germanium crystals are oriented and cut into thin wafers, then polished into substrates 140 μm thick. Gallium arsenide and ternary compounds are deposited in thin film form to create a photovoltaic device. A coverglass and backside metallization is applied, and a solar cell has been created. The primary advantages of GaAs/Ge cells over those of silicon for satellite use are much higher efficiencies at end-of-life power, much lower cost at the system level as booster cost is significant and less structure that has to be orbited, and more radiation resistance. The 66 operating satellites of Motorola's Iridium worldwide cellular communication constellation utilized Eagle-Picher's substrates. Other "Internet-in-the-sky constellations" are now proposed, and the system-level economic analysis indicates that many millions of dollars can be saved with a second-generation GaAs/Ge photovoltaic cell power system.

11.1. New Product Introductions.

The most publicized new product is the silicon germanium chip from IBM. In 1996, IBM had an estimated $7 billion in chip revenue and by 2001 SiGe chips could account for 10% of these sales. Currently SiGe is touted as a low-price, high-speed device designed to substitute for GaAs chips in certain applications, such as cellular telephones. The hetrojunction bipolar transistor technology for SiGe has become practical only since 1989, and now the uses are multiplying into direct broadcast satellite, automobile radar systems, and personal digital assistants.

Several manufacturers have begun production of SiGe chips. During 2002, TriQuint Semiconductor, Inc., took over the design, development, marketing and sales of certain IBM semiconductor products used in wireless phones and other communication applications.

An optional Raytheon Night Driver™ System using Ge-chalcogenide lenses was made for the 2000 model Cadillac Deville. It allowed the driver to see 3 to 5 times farther than using low beam headlights. All were sold out.

Two automobile manufacturers have incorporated germanium-based night vision systems in limited editions in their product lines. At least one manufacturer has announced a similar system for buses and trucks (61). These night vision systems are also finding use in firefighting systems for thermal imaging. Germanium thermal imaging can be used to detect hot spots team members, and endangered individuals in smoky environments (62).

Argentium Sterling, an alloy composed of 92.5% silver, 6.3% copper, and 1.2% germanium has been discovered and patented by Middlesex University and a company in New Jersey has been licensed to produce the alloy. This alloy has tarnish-resistant properties and virtually eliminates firescale.

Other new applications recently announced include germanium emitters for cleanroom ionization, Ge-containing superconductors, Ge substrates for ultra-bright-light-emitting diodes, and other semiconductor uses, and a revival of the 1960s Ge-transistorized "wah-wah" pedal for rock bands.

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