SILICON

1. Introduction

Silicon [7440-21-3], Si, from the Latin *silex, silicis* for flint, is the fourteenth element of the Periodic Table, has atomic wt 28.083, and a room temperature density of 2.3 gm/cm^3. Silicon is brittle, has a gray, metallic luster, and melts at 1412°C. In 1787 Lavoisier suggested that silica (qv), of which flint is one form, was the oxide of an unknown element. Gay-Lussac and Thenard apparently produced elemental silicon in 1811 by reducing silicon tetrafluoride with potassium but did not recognize it as an element. In 1817 Berzelius reported evidence of silicon occurring as a precipitate in cast iron. Elemental silicon does not occur in nature. As a constituent of various minerals, eg, silica and silicates such as the feldspars and kaolins, however, silicon comprises about 28% of the earth's crust. There are three stable isotopes that occur naturally and several that can be prepared artificially and are radioactive (Table 1) (1).

Silicon technology has proceeded along two rather diverse paths. The first encompasses metallurgical-grade silicon, a low purity, low cost material used in large quantities in metallurgical applications and as a feedstock for the preparation of the silicon compounds (qv) used in the silicone industry. The other path encompasses high purity silicon. The latter is also referred to as semiconductor-, electronic-, or transistor-grade silicon, and most impurity levels are in the parts per billion (ppb) range. High purity silicon is much more expensive than the metallurgical grade only because of the additional steps required to remove unwanted impurities. This quality silicon is used primarily in the manufacture of semiconductor devices such as integrated circuits (qv). High purity silicon is used in much smaller quantities than the metallurgical grade and is generally converted into single-crystal form before use. The demand for high purity silicon has risen through the years as the volume of silicon-based semiconductor devices has increased.

The chemical properties of silicon are not particularly sensitive to small amounts of impurities and have mostly been determined using low purity material. However, many of the mechanical, electrical, and optical properties are substantially altered by the level of impurities. These have been reexamined in detail since high purity silicon first became available in the late 1940s.

2. Crystal Structure

At atmospheric pressure, silicon has a diamond cubic structure, ie, two interpenetrating face-centered cubes displaced 1/4, 1/4, 1/4 from each other. When subjected to ca 11 GPa (~110,000 atm) hydrostatic pressure, the diamond structure is converted to a body-centered tetragonal lattice. If a shear component of force is present, the transition pressure is reduced somewhat. Between about 15 and 40 GPa, a simple hexagonal structure is stable; above that, a close-packed hexagonal structure is stable. In addition, a metastable, body-centered cubic form is observed as the pressure is reduced from 10 to 0 GPa (2). Silicon produced at temperatures below about 500°C by vapor deposition is generally amorphous. However, when it is heated to a somewhat higher temperature, crystallization occurs.

In the early literature a hexagonal form stable at atmospheric pressure and thought to be analogous to the graphitic form of carbon was reported, but its existence has never been verified. Additional crystallographic data is given in Table 2.

Under most circumstances the equilibrium shape of silicon crystals is octahedral, ie, the slowest-growing faces are $\langle 111 \rangle$. However, external conditions can radically alter that shape. For example, when growth is from the vapor, concentration gradients in the gas stream may affect the shape, and when growth is from the melt, the shape is primarily determined by thermal gradients in the melt.

3. Physical Properties

Unlike structural materials where properties are generally given for polycrystalline samples, many of the properties of the high purity silicon required for the manufacture of semiconductor devices are measured on single-crystal samples. For this reason, even though silicon was isolated in the early 1800s, most of the values for pure silicon have been measured since the introduction of single-crystal silicon growing techniques in the 1950s.

For cubic crystals, which include silicon, properties described by other than a zero- or a second-rank tensor are anisotropic (3). Thus, in principle, whether or not a particular property is anisotropic can be predicted. There are some properties, however, for which the tensor rank is not known. In addition, in very thin crystal sections, the crystal may have two-dimensional characteristics and exhibit a different symmetry from the bulk, three-dimensional crystal (4). Table 3 is a listing of various isotropic and anisotropic silicon properties. Table 4 gives values for the more common physical properties and for some of the thermodynamic properties. Figure 1 shows some thermal properties.

Molten silicon is not a semiconductor, and has no commercial use, although because of the high heat of fusion, it has been considered as a heat storage medium. The liquid (molten) silicon properties summarized in Table 5 are nevertheless of importance because these affect single-crystal growth, an operation through which essentially all semiconductor-grade silicon must pass.

3.1. Electrical Properties.

Silicon (20) is a semiconductor and thus the electrical conductivity, σ, is determined by contributions from both electrons and holes, ie,

$$\sigma = q(\mu_n n + \mu_p p) \tag{1}$$

where q = charge on an electron, μ = carrier mobility in cm^2/(V·s), n = density of free electrons (electrons/cm^3), and p = density of free holes. For an absolutely pure semiconductor, $n = p \equiv n_i$. For silicon, n_i is given by equation 2:

$$n_i \simeq \left(1.5 \times 10^{33} T^3 \exp(E_g/kT)\right)^{1/2} \tag{2}$$

where T = temperature in K, k is Boltzmann's constant, and E_g is the band gap in eV. The value of the indirect band gap in silicon can be approximated by equation 3:

$$E_g = 1.16 + 3 \times 10^{-5} T - 9 \times 10^{-7} T^2 + 10^{-9} T^3 - 4 \times 10^{-13} T^4 \tag{3}$$

More precise coefficients are available (20). At room temperature, $E_g \simeq 1.12\,\text{eV}$ and $n_i \simeq 1.4\times10^{10}/\text{cm}^3$. Both hole and electron mobilities decrease as the number of carriers increase, but near room temperature and for concentrations less than about 10^{16} there is little change, and the values are ca $1400\,\text{cm}^2/(\text{V}\cdot\text{s})$ for electrons and ca $475\,\text{cm}^2/(\text{V}\cdot\text{s})$ for holes. These numbers give a calculated electrical resistivity, the reciprocal of conductivity, for pure silicon of ca 230,000 Ω·m. As can be seen from equation 6, the carrier concentration n_i increases exponentially with temperature, and at 700°C the resistivity has dropped to ca 0.1 Ω·m.

Instead of depending on the thermally generated carriers just described (intrinsic conduction), it is also possible to deliberately incorporate various impurity atoms into the silicon lattice that ionize at relatively low temperatures and provide either free holes or electrons. In particular, Group 13 (IIIA) elements (*n*-type dopants) supply electrons and Group 15 (VA) elements (*p*-type dopants) supply holes. Over the normal doping range, one impurity atom supplies one hole or one electron. Of these elements, boron (*p*-type), and phosphorus, arsenic, and antimony (*n*-type) are most commonly used. When enough impurity atoms are present for holes or electrons from these impurities to overshadow the thermally generated carriers from the silicon itself, conduction is referred to as extrinsic. Impurity concentration is commonly expressed in atoms of impurity per cm^3 of host material. When used as a semiconductor material, purity is sometimes described by the material resistivity, even though resistivity depends on the excess concentration of one doping type impurity over the other (1000 Ω·m silicon is considered very pure; 0.001 Ω·m is very impure). Because of the solubility limit of most impurities in silicon, 0.001 Ω·m is about as low a resistivity as is observed. The impurity concentration required in a silicon single crystal to be used for semiconductor device manufacture depends on the kind of devices to be made and may range from about 10^{14} to 10^{17} atoms/cm^3 and give resistivities of from ca 100 to 0.1 Ω·m.

Carriers can also be generated in a semiconductor by the absorption of light or injected into the semiconductor from a p–n or Schottky junction. In either case, as soon as the source is removed the density of those excess carriers begins to decrease exponentially with time. The time it takes for the density to be reduced to $1/e$ of the original value is defined as the carrier lifetime, τ. For silicon, τ is typically in the microsecond range.

The general behavior of resistivity vs temperature is shown in Figure 2. In the region where extrinsic conduction dominates, resistivity increases with temperature because the carrier mobility decreases with temperature and the carrier concentration remains constant. At some point, however, the temperature becomes high enough for the thermally generated carriers to dominate, and the resistivity drops as more and more carriers are generated (the exponential increase in n_i of eq. 6). The relation between impurity concentration and resistivity at room temperature is shown in Figure 3 (21). The difference between *n*- and *p*-type curves arises because of the difference between hole and electron mobilities.

In bulk material, the resistivity is independent of crystal orientation because silicon is cubic. However, if the carriers are constrained to travel in a very thin sheet, eg, in an inversion layer, the mobility, and thus the resistivity, become anisotropic (4). Mobility is also sensitive to both hydrostatic pressure and uniaxial tension and compression, which gives rise to a substantial piezoresistive effect. Because of crystal symmetry, however, there is no piezoelectric effect. The resistivity gradually decreases as hydrostatic pressure is increased, and then abruptly drops several orders of magnitude at ca 11 GPa (160,000 psi), where a phase transformation occurs and silicon becomes a metal (22). The longitudinal piezoresistive coefficient varies with the direction of stress, the impurity concentration, and the temperature. At about 25°C, given stress in a ⟨100⟩ direction and resistivities of a few hundredths of an Ω·m, the coefficient values are 500–600 m^2/N (50–60 $\mathrm{cm}^2/\mathrm{dyn}$).

3.2. Radiation Effects. Gamma radiation produces free carriers much as does visible light (23). High energy protons and electrons produce defects that reduce minority carrier lifetime according to equation 4:

$$1/\tau_f = 1/\tau_0 + k\phi \tag{4}$$

where τ_f is the lifetime after irradiation with a fluence ϕ, τ_0 is the original lifetime, and k is a radiation damage constant. Neutrons produce deep-level defects that not only degrade lifetime as in equation 4, but also increase resistivity through the removal of carriers, as described by equation 5.

$$N = N_0 - K\phi \tag{5}$$

where N_0 is the initial carrier density, N the density after irradiation, and K a different radiation damage constant. All of the damage-constant values are dependent on the kind and energy of the irradiation, the kinds of impurities in the silicon, and the temperature of the silicon during irradiation. Moreover, many of the defects anneal out at higher temperatures, thereby reducing the effects of irradiation.

Neutrons also transform some of the silicon atoms to phosphorus through the following reaction 6:

$$^{30}\mathrm{Si} + n \xrightarrow{31} \mathrm{Si} + \gamma \xrightarrow{31} \mathrm{P} + \beta \tag{6}$$

This reaction is occasionally used for doping crystals uniformly after they have been grown. The process is called transmutation doping (24).

3.3. Optical Properties. The optical transmissivity of silicon is shown in Figure 4**a**. The general characteristic, shared as well by other semiconductors, is that at wavelengths shorter than some critical value defined by the band gap energy, optical absorption generates free carriers and the transmissivity is very low. Figure 4**b** shows the absorption coefficient for the wavelength range from 0.5–1 μm. The absorption coefficient changes several orders of magnitude over that wavelength range. This change is not nearly as abrupt as it is in direct band gap materials such as gallium arsenide, GaAs. Also, because Si is an indirect band gap material, it cannot be used for conventional light-emitting diodes (see Light Generation, Light-Emitting Diodes). The free-carrier generation, shared by both direct and indirect band gap materials, leads to the production of electrical current in photovoltaic devices such as solar cells. The closer the wavelength band of maximum absorption matches the emission peak of the light source, the greater the theoretical maximum efficiency of the cell. For silicon, the match between it and the sun's spectrum is quite good.

For wavelengths having photon energies less than that corresponding to the band gap, the transmissivity is substantial, but as wavelengths continue to increase, both impurity absorption bands and the gradually increasing free-carrier absorption reduce transmissivity. There are also a number of lattice absorption bands, the most pronounced of which is at 16.13 nm. Silicon is often used as an infrared optical element because of the good infrared transmissivity in the 1–8-μm region. Owing to the high index of refraction, shown in Figure 5, reflection losses are about 30% per reflecting surface. However, by using antireflection coatings such as silicon monoxide, SiO, those losses can be minimized. Silicon surfaces take a good optical finish. The sawing, grinding, and polishing operations are similar to those for glass.

4. Chemical Properties

Silicon (26), which resembles metals in its chemical behavior, generally has a valence of +4. In a few compounds it exhibits a +2 valence, and in silicides it exists as a negative ion and largely violates the normal valency rules. Silicon, carbon, germanium, tin, and lead comprise the Group 14 (IVA) elements. Silicon and carbon form the carbide, SiC (see CARBIDES). Silicon and germanium are isomorphous and thus mutually soluble in all proportions. Neither tin nor lead reacts with silicon. Molten silicon is immiscible in both molten tin and molten lead.

Silicon forms many compounds that are analogous to those of carbon and thus sometimes appears to give rise to an inorganic equivalent of carbon-based organic chemistry. However, the known silicon compounds (qv) are far fewer and much less complex than those of carbon. One example of these silicon-based compounds is the silane series, eg, SiH_4, Si_2H_6, Si_3H_8, and Si_4H_{10}, which corresponds to the paraffin hydrocarbon series. The silanes react explosively with air and are very poisonous (see SILICON COMPOUNDS, SILANES). Monosilane, SiH_4, however, can be safely decomposed at a few hundred degrees centigrade to give silicon and, provided the concentrations are carefully controlled, can be used to deposit SiO_2 layers on hot surfaces through the following reaction:

$$O_2 + SiH_4 \longrightarrow SiO_2 + 2\,H_2$$

Siloxanes are oxygen-containing silanes that appear at first glance to be similar to oxygen-containing hydrocarbon equivalents, but are really much different. Compounds in which silicon directly attaches to an organic radical also form, giving rise to a large number of organosilicon compounds.

Silicon reacts at elevated temperatures with the halogens, forming $SiCl_4$, SiI_4, $SiBr_4$, and SiF_4. There is also a series of halogen-substituted silanes such as trichlorosilane, SiH_3Cl, and dichlorosilane, SiH_2Cl_2. Both $SiCl_4$ and SiH_3Cl are relatively easy to make, purify, and reduce to silicon. These are the silicon compounds most often used as feedstocks in the manufacture of high purity silicon.

Oxygen forms strong bonds with silicon. There are two oxides, quartz or silica, SiO_2, and silicon monoxide, SiO, each of which can exist at room temperature as crystalline or vitreous material; numerous silicates; and almost endless silicone variations. In silica the bond energy is 25.8 kJ (108 kcal) and the bond length 0.163 nm. The nature of the silicon–oxygen bond is of great importance to the semiconductor industry because silicon–oxygen bonding at the oxide–silicon interface of SiO_2-protected silicon devices has a significant effect on silicon semiconductor device performance. Silicon oxidizes to amorphous SiO_2 in an air or oxygen atmosphere, even at room temperature. However, this reaction depends on the diffusion of silicon from the Si–SiO_2 interface to the oxide surface, and at room temperature the oxide thickness is self-limited to 2–3 nm. At higher temperatures the rate of oxide growth (thermal oxide) increases substantially, as shown in Figure 6.

For the manufacture of silicon semiconductor devices, oxide thicknesses of from <10 to >1000 nm are required on slices of single-crystal silicon. These oxide layers are formed at elevated temperatures, generally at about 1000°C, in an atmosphere of either oxygen or steam. Usually the oxidation is at atmospheric pressure, but sometimes, to speed the oxidation rate, pressures of several atmospheres are used. Oxidation consumes a silicon thickness equal to about 0.4 the thickness of the oxide produced (grown). The thickness of the oxide, X (27) is approximately given by equation 7:

$$X^2 + AX = B(t + \tau) \tag{7}$$

where A and B are rate constants, τ is a constant involving the initial oxide thickness, and t is the oxidation time. Initially X varies linearly with time, but as oxidation continues, the rate slows and X varies as $t^{1/2}$. The values for A and B depend on temperature, pressure, the oxidant, the crystal orientation of the silicon surface being oxidized, and the amount and kind of impurity in the silicon.

Oxygen also dissolves in the silicon crystal lattice, forming SiO_x, which may radically affect the electrical properties of the silicon. Oxygen is usually unintentionally introduced during the crystal-growing operation in concentrations up to the solubility limit (ca 2.5×10^{18} atoms/cm^3). When oxygen-containing silicon is annealed in the 450°C range, the OSi complexes become donors and contribute to electrical conductivity. At higher temperatures, larger, electrically inactive clusters form and sometimes cause crystal defects. Above ca 1200°C, the clusters begin to dissolve and the oxygen is redispersed (19). At room temperature and below, silicon appears relatively inert, partly because of the rapid formation in air of a thin layer of protective oxide, SiO_2.

Silicon is virtually insoluble in any single acid but can be dissolved in a two-component, two-stage operation in which one acid component oxidizes the surface and the other etches away the oxide (28). For this purpose, aqueous solutions of HNO_3 and HF are generally used. If a hydrated oxide is formed, eg, by the reaction of silicon and potassium hydroxide or hydrazine, it can be removed with water and a suitable complexing agent (19). Ethylenediamine and isopropyl alcohol are often used with KOH and pyrocatechol with hydrazine. In most proportions the HNO_3–HF–H_2O system etches isotropically and is used for chemically polishing silicon. The others are anisotropic and have very low etch rates on

$\langle 111\rangle$ faces. The anisotropy can be very pronounced. If there are no ledges to promote etching, and if the constituent proportions are properly adjusted, ratios of up to 400 between the $\langle 111\rangle$ and other faces can be obtained. Anisotropic etching is used in the manufacture of some silicon-integrated circuits and for the micromachining of silicon (29). Etching, again usually using HNO_3–HF–H_2O in various proportions, can be used to delineate crystal defects.

Electrolytic (anodic) etching of silicon occurs in HF solutions (19). Using concentrated HF, the silicon is dissolved in the divalent state:

$$\mathrm{Si}^0 + 2\,\mathrm{HF} \longrightarrow \mathrm{SiF}_2 + 2\,\mathrm{H}^+ + 2\,e^-$$

In dilute HF solutions and higher anodic voltages, the silicon is dissolved in the tetravalent state:

$$\mathrm{Si}^0 + 4\,\mathrm{H_2O} \longrightarrow \mathrm{Si(OH)}_4 + 4\,\mathrm{H}^+ + 4\,e^-$$

Free radicals such as F· can be used to etch silicon at ambient temperature. The radicals are formed by dissociating compounds such as CF_4 in a plasma. Thus,

$$\mathrm{CF_4(plasma)} \longrightarrow \mathrm{CF_3} + \mathrm{F}\cdot$$

$$4\,\mathrm{F}\cdot + \mathrm{Si} \longrightarrow \mathrm{SiF_4}$$

Plasma etching is widely used in semiconductor device manufacturing to etch patterns in thin layers of polycrystalline silicon often used for metal oxide semiconductor (MOS) device gates and interconnects.

5. High Purity Silicon Preparation

Early processes for providing quantities of high purity silicon started with the metallurgical grade of silicon produced by the reduction of silica and coke in an electric arc furnace and the attempts to purify it metallurgically (30). A specific process described as early as 1919 and used during World War II to produce silicon for microwave diodes made use of the fact that most impurities in a melt are segregated at the grain boundaries when the melt freezes. If the frozen polycrystalline agglomerate is crushed, most of the fracturing occurs at the grain boundaries. If the crushed mass is then treated with appropriate acids, many of the impurities that were segregated at the grain boundaries could be leached out. Another related method that was developed in the early 1940s makes use of the fact that the last portion of an ingot to freeze generally has a higher concentration of impurities than the first part. If freezing is constrained to move from one end of the ingot to the other and the ingot is of uniform cross section, the impurity concentration, C (31), as a function of g, the fraction of ingot solidified, is given by equation 8:

$$C(g) = kC_0(1-g)^{k-1} \tag{8}$$

where C_0 is the initial impurity in the melt and k is the distribution coefficient of the impurity in question. When k is <1, as is generally the case, impurities are concentrated in the last end to freeze, so net purification occurs if that end is cut off and discarded. Remelting the remainder and repeating the process improves purity, but this process is quite unwieldy. Float zone refining, a variant of zone refining (qv) applicable to silicon because it keeps the molten silicon zone from contacting possible contaminants, is shown in Figure 7. This procedure provides a more convenient path to purification by allowing a molten zone of length δ to be moved the length of the ingot, x. In that case, instead of equation 8, equation 9 must be used (10).

$$C(x) = C_0(1 - (1 - k)e^{-kx/\delta}) \tag{9}$$

The length of the zone and the diameter of the rod are chosen in such a way that surface tension and interactions between circulating electric currents in the molten zone and the radio-frequency (r-f) field from the surrounding induction coil keep the molten zone in place. Initially, additional purification can be obtained by making more sweeps of the zone. Eventually, however, more sweeps do not remove any additional impurities. The limiting profile is given by equation 10:

$$C(x) = Ae^{Bx} \tag{10}$$

where A and B are constants that depend on the value of k and the ingot length (31). Values of k_e, the equilibrium distribution coefficient, for various impurities in silicon are given in Table 6. The k of equations 2 and 3 differs from k_e if freezing is very rapid, but when using float zone refining for purification, the freezing rate is kept low, then $k = k_e$.

To produce the purity of silicon required for most semiconductor applications in the necessary quantities, a different approach is used (33). Metallurgical-grade silicon is first converted to a silicon compound that can be easily purified. After extensive purification, that compound is reduced to silicon by using a high purity reducing agent. Silicon tetrachloride, $SiCl_4$; trichlorosilane, $SiHCl_3$; and silane, SiH_4, are the silicon compounds most often used. In the earliest commercial process, which was introduced by DuPont, extensively distilled silicon tetrachloride was reduced by high purity zinc to give Si and $ZnCl_2$. Reduction was carried out in a fused silica tube heated in an electric furnace to about 950°C. The silicon produced was generally in the form of polycrystalline needles from 2.5–5 cm long. Difficulties in handling molten zinc, the clogging of exit lines by $ZnCl_2$, and the poor packing efficiency of the needles, led to the investigation of many other processes over the years.

The purification method that has become a near-standard is the Siemens process, where hydrogen reduces $SiCl_4$ or $SiHCl_3$ on the surface of a resistance-heated (to about 1150°C) high purity silicon rod. The rod is usually U-shaped to reduce the height of the furnace. The result is a silicon ingot several cm in diameter and ≥ 2 m long. It is tempting to write the silicon tetrachloride–hydrogen reaction as

$$SiCl_4 + 2\,H_2 \longrightarrow Si^0 + 4\,HCl$$

but in fact there are many other reaction products. Depending on the temperature and concentrations, many compounds coexist in the Si$-$Cl$-$H system. These include $SiCl_2$, SiH_2Cl_2, $SiHCl_3$, and a series of long-chain polymeric materials, some of which are explosive. In order to improve process efficiency, silicon manufacturing plants have provisions for reclaiming unreacted feed gases and many of the reaction products. A flow sheet for a facility that starts with metallurgical-grade silicon is shown in Figure 8. In the case illustrated, the fluidized bed is adjusted to produce primarily trichlorosilane, because trichlorosilane is one of the easiest silicon compounds to purify and reduce efficiently. Rather than starting with metallurgical-grade silicon as in Figure 8 and manufacturing the intermediate $SiCl_4$ or $SiHCl_3$, some high purity silicon manufacturers take advantage of the large-scale operations of silicone manufacturers and buy $SiCl_4$ or $SiHCl_3$ from them.

5.1. Crystal Growth. Most high purity silicon is used in the manufacture of semiconductor devices, and most such devices are made from single-crystal silicon. Thus the process of growing single crystals of silicon has been studied extensively since the 1950s. A number of processes are available, but the most common is the pulling technique first described by Teal and Little in 1950 (34). This is an adaptation of a much earlier crystal growing method for studying the speed of crystallization of metals (35), called the Czochralski method. The pulling process is shown schematically in Figure 9. Silicon, surrounded by an inert gas atmosphere, is first melted in a fused silica container. Then, the bottom end of a single-crystal silicon seed, capable of being both rotated and pulled up from the melt, is dipped into the melt and slowly withdrawn as silicon freezes on it. The freezing (growth) rate, normally on the order of cm/h, is controlled by a combination of melt temperature, radiation from the growing crystal, and conductive heat losses through the seed. Crystals as small as a few mm in diameter and as large as 300 mm in diameter have been grown by this process. Lengths vary according to equipment design and crystal diameter, but may be as much as ≥ 2 m for 100-mm diameter crystals and as little as 50$-$60 cm for 300-mm diameter crystals.

The principal difficulty with Czochralski silicon crystal growing is that it is difficult to maintain a container of reactive molten silicon free of contamination for the several hours required to grow a crystal. The contaminants arise from the fused silica container, which is slowly dissolved by the molten silicon, from impurities in the inert atmosphere gas, and from the vaporization of hot portions of the furnace. For applications requiring the highest purity, float zone crystal growing, which uses no crucible and physically uses the same equipment as was shown in Figure 2, is sometimes used instead of crystal pulling. A polycrystalline rod with a single-crystal seed at one end is held vertically, and the heated molten zone is caused to traverse the length of the rod, starting at the end that contains the seed. The molten zone never contacts anything but silicon. The chamber size, and hence the volume of inert gas, can be kept comparatively small; the chamber walls can be kept relatively cool.

Most semiconductor applications require thin, flat sections of crystal having damage-free surfaces for subsequent processing. Both the Czochralski and float zone methods produce long rods from which slices must be cut and subsequently lapped and polished. In an attempt to circumvent these steps, various modifications of melt growth have been proposed in order to grow single-crystal ribbons directly. The work started in the early 1960s concentrated on dendrites and on growth in a $\langle 211 \rangle$ direction through a shaped orifice (36). Neither the dendrites nor the dendrite webs that followed were of sufficient quality for most uses, and shaped crystals could not be grown thin enough to be of practical use. In the mid-1970s, the realization that reasonably efficient solar cells could be made from poorer quality silicon material than was usable for transistors and integrated circuits, combined with a renewed search for low cost cells, led to renewed studies of sheet growth (see SOLAR ENERGY). One of the more promising approaches has been edge-defined growth, where a silicon carbide die having a cross section equal to that of the desired crystal is used. The lower end of the die is immersed in molten silicon in such a way that surface tension can draw molten silicon to the top of the die. The crystal is then pulled from that small reservoir and can grow no larger in cross section than the silicon supply at the top of the die.

Single-crystal silicon can also be grown from various fluxes and by a combination of electrolysis and fluxes at temperatures well below the melting point of pure silicon (37). The main disadvantages are the inclusion of the flux in the crystal and the poor crystal quality. Potential advantages are a decrease in growth temperature and purification during electrolysis.

Since the mid-1990s vapor-phase growth at temperatures well below the melting point is used widely for adding thin single-crystal layers to single-crystal slices. This process is referred to as epitaxy. Vapor-phase growth allows thin layers of high resistivity to be overgrown on low resistivity slices. Moreover, doping impurities in the vapor-grown portion can be rapidly changed, allowing the sequential growth of thin layers having different resistivities. The method of transport of silicon to the growing interface may be by direct evaporation, ie, molecular-beam epitaxy, or by chemical means (19). Using chemical transport, any of the reactions discussed for manufacturing semiconductor-grade silicon may be used. The thermal decomposition of silane and the hydrogen reduction of principally $SiCl_4$, $SiHCl_3$, or SiH_2Cl_2 are used. Deposition rates, which depend on a deposition temperature of typically ca $1000-1100°C$, are generally from tenths to a few μm/min. Occasionally, polycrystalline or amorphous silicon layers, often on nonsilicon surfaces such as glass or SiO_2, are required, in which case lower deposition temperatures are used.

For adding doping impurities during vapor-phase growth, a gaseous or easily vaporizable liquid compound is metered, added to the silicon source gas stream, and reduced along with the silicon compound. Typical examples are diborane, B_2H_6; phosphine, PH_3; and boron tribromide, BBr_3.

6. Economic Aspects

The 2005 world production of silicon metal was estimated at about 686×10^3 metric tons. The average selling price was about \$81.92/lb (38). Principal suppliers are listed in Table 7.

Estimated value of silicon metal and alloys (excluding semiconductor-grade silicon) produced in the United States in 2005 was about \$412 million.

The main consumers of silicon metal were producers of aluminum and aluminum alloys and the chemical industry. The semiconductor industry, which manufactures chips for computers from high-purity silicon, accounted for only a few percent of silicon demand.

The American Chemistry Council estimated a 4.5% gain in domestic chemical volumes in 2004, moderating to 3.8% in 2005, as a result of improving economic recovery in 2004 within the United States. Globally, chemical output volumes were expected to increases 5.0% and 4.3% in 2004 and 2005, respectively (40). Demand for silicon by the U.S. aluminum castings industry was expected to mirror the 6.4% increase in aluminum casting shipments forecasted in 2005 (41).

As a rough indicator of high-purity silicon demand, world production of polycrystalline silicon was forecasted to increase by 16% to 27,000 t in 2004. Output of semiconductor-grade material was expected to rise by 19% to 19,350 t and that of solar battery-grade material by 13% to 7,650 t (42).

Demand for microsilica comes from the cement industry. Worldwide demand for cement was projected to rise 4.1% annually through 2006 to 2.1 billion metric tons, although advances were expected to be less robust in more developed areas such as Japan, the United States, and Western Europe (43).

Silicon metal imports rose by 30% to 167,000 t from 128,000 t, and 43% in value of $314 million from $220 million compared with those in 2003. Imports increased in all silicon metal categories, the largest amount of which was in the “99.00% to 99.99% silicon” category. Brazil was the leading source of the “99.00% to 99.99% silicon” import category at 41%, followed by South Africa at 24%. This category accounted for 55% of the total value for silicon metal imports, an increase of 36% from those in 2003 (38).

7. Analytical Methods

There are a variety of wet chemistry procedures for analyzing silicon, depending on the silicon concentration and the composition of host material (44). Generally, any silicon is first converted to silica or silicic acid. If the material is organic, this can be done by ashing; otherwise, the use of a fluxing agent such as Na_2CO_3 or $Na_2Br_4O_7$, followed by an acid treatment to precipitate gelatinous silicic acid, is required. Quantitative analysis by, for example, colorimetry can be done at this point, or the amount of SiO_2 can be determined by the amount of precipitate that dissolves in HF.

Silicon has strong optical emission lines at 251.6113 and 288.1579 nm that can easily be detected by emission spectrography and that give sensitivities in the 1–100-ppm range. For nondestructive analysis, either x-ray diffraction or x-ray fluorescence may be used (see SPECTROSCOPY; X-RAY TECHNOLOGY).

When considering pure silicon, there is much more emphasis on detecting trace impurities in the silicon than on the detection of silicon itself. Whereas optical spectroscopy, secondary ion mass spectroscopy (sims), x-ray fluorescence, neutron-activation analysis, and Auger spectroscopy have all been used, indirect electrical measurements generally provide the greater sensitivity required to detect impurities in the parts per billion (ppb) range. For example, electrical resistivity measurements allow the detection of <1 ppb of an electrically active impurity, although the impurity itself cannot be identified. There are also various measurements that can be made on diodes, eg, deep-level transient spectroscopy (dlts), that allow the presence of impurities in the ppb range to be inferred.

The distribution of impurities over a flat silicon surface can be measured by autoradiography or by scanning the surface using any of the methods appropriate for trace impurity detection (see TRACE AND RESIDUE ANALYSIS). Depth measurements can be made by combining any of the above measurements with the repeated removal of thin layers of silicon, either by wet etching, plasma etching, or sputtering. Care must be taken, however, to ensure that the material removal method does not contaminate the silicon surface.

8. Health and Safety Factors

Elemental silicon is quite inert. In air, silicon is only classified as a nuisance particulate (45,46) having a threshold limit value (TLV) of 10 mg/m^3; respirable fraction is 5 mg/m^3. However, SiO_2 dust, particularly that of crystalline quartz, is considered hazardous. Many silicon compounds are poisonous, and some, such as the silanes, are highly explosive as well. Compounds such as $SiCl_4$, $SiHCl_3$, and $SiBr_4$ decompose in the presence of moisture, forming SiO_2 and the corresponding acid. If such compounds are breathed, the acid-forming reaction takes place in the moist respiratory tract and the result is similar to that of directly breathing the acid fumes.

9. Uses

The main uses for silicon are in the aluminum alloys and chemical industries. The semiconductor industry, which manufactures chips for high purity silicon, accounts for only a small portion of the demand.

9.1. Semiconductors and Electronics. Silicon Genesis Corp is working on technology that transfers films of stressed silicon onto silicon-on-insulator substrates, which results in defect-and germanium-free substrates. The company believes these silicon substrates will find use in the “next generation” semiconductor applications (47).

Liquid crystalline displays using a silicon substrate have been reported (48).

9.2. Nanotechnology. A new method has been reported that allows silicon to be patterned with functional organic groups through selective deposition of alcohol, amines, and proteins on silicon surfaces. Such layering could find application in nanotechnology and sensors (49). A method has been devised for making electrical contact to nanometer-sized semiconductors circuit elements using metallic wires of the same dimensions as the semiconductor. The nanosized entities are brought together by selectively converting segments of a silicon nanowire to metallic nickel silicide. Researchers at Harvard believe that this technology will enable the fabrication of a multifunctional complex nanoscale electronic and optoelectronic devices (50, 51).

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W. R. Runyan
Texas Instruments, Inc.

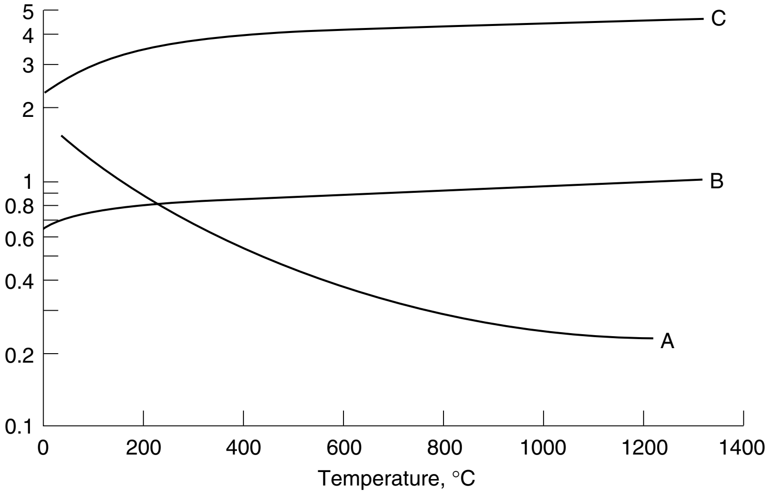


Fig. 1. Thermal properties of silicon (14). A represents thermal conductivity in W/(cm·K); B, specific heat in J/(g·K) (to convert J to cal, divide by 4.184); and C, thermal expansion coefficient $\times 10^6\,\mathrm{K}^{-1}$.

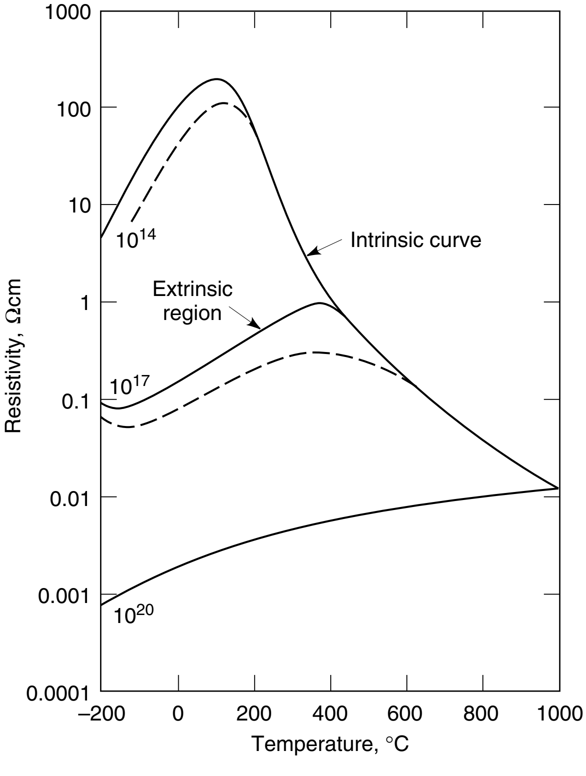


Fig. 2. Calculated silicon resistivity vs temperature for the impurity (doping) levels shown, where (—) is *p*-type, (– – –), *n*-type. Left of the peaks is the extrinsic region where the resistivity is determined by the doping level. To the right of the peaks is the intrinsic region, where the resistivity is determined by thermally generated carriers.

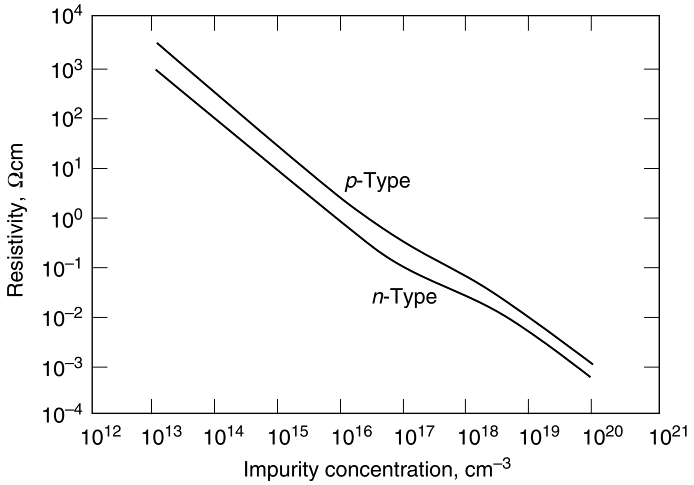
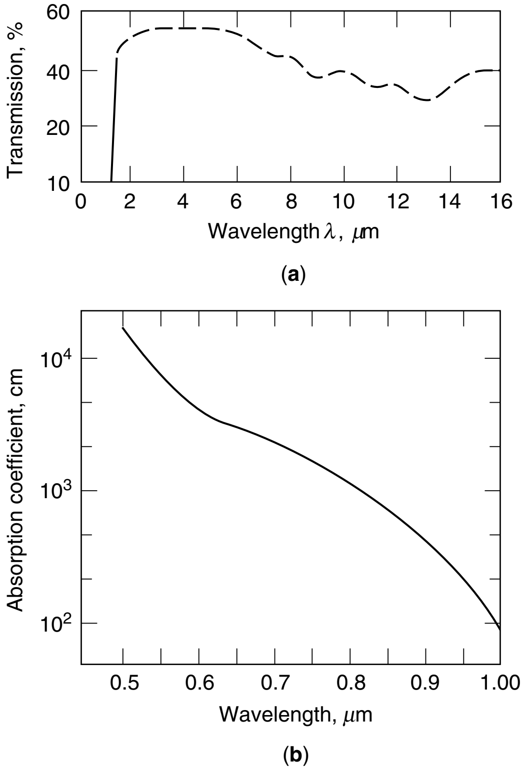


Fig. 3. Impurity concentration vs resistivity at room temperature (21). These curves are for phosphorus (*n*-type) and boron (*p*-type). Other Group 13 (IIIA) and 15 (VA) impurities behave similarly. (Courtesy of the *Bell System Technical Journal* (1960).)



(**a**)

(**b**)

Fig. 4. Optical properties of silicon: (a) transmissivity vs wavelength, (b) shortwavelength absorption coefficient where the transmissivity increases sharply with wavelength.

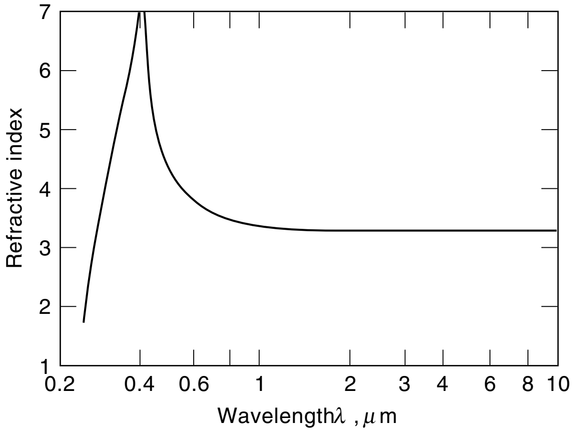


Fig. 5. Refractive index of silicon at room temperature (25).

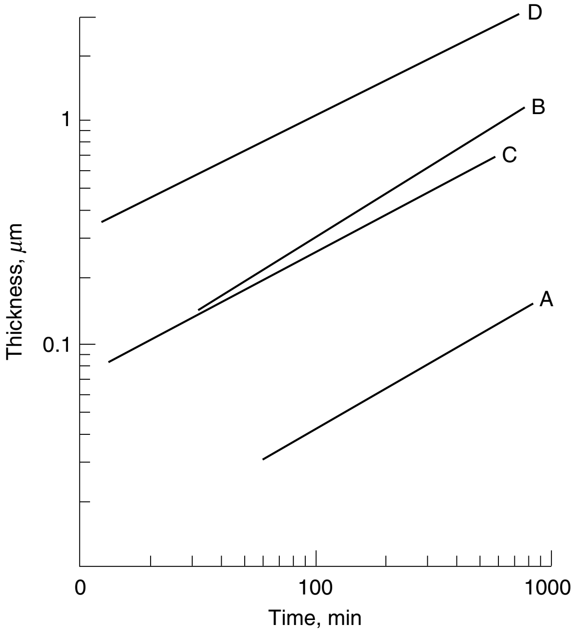


Fig. 6. Thermal oxidation rates for silicon single-crystal $\langle 111 \rangle$ surfaces: A at 900°C in dry O_2; B at 900°C in steam; C at 1200°C in dry O_2; and D at 1200°C in steam.

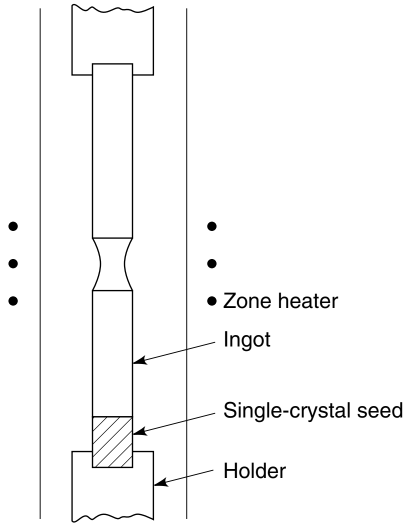


Fig. 7. Float zone purification of silicon.

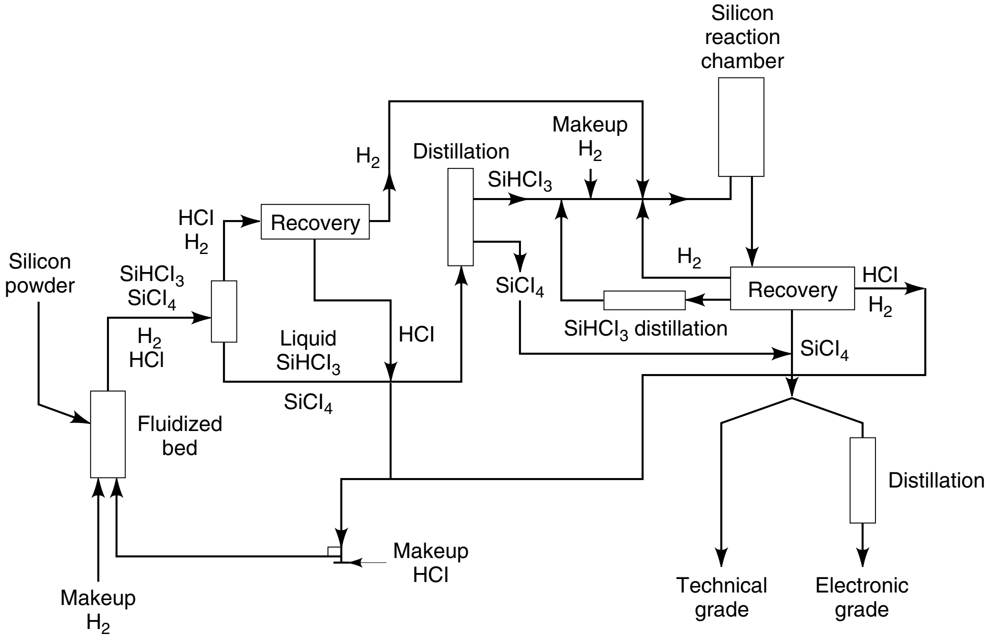


Fig. 8. Flow sheet for silicon manufacturing.

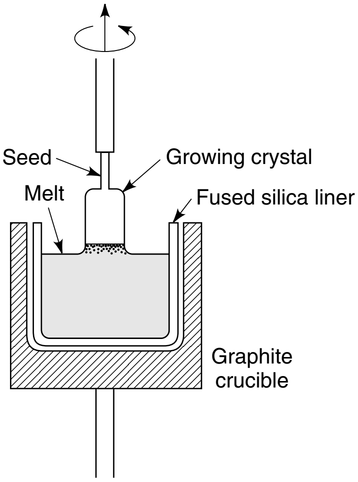


Fig. 9. Crystal pulling from the melt.

Table 1. **Isotopes of Silicon**

Isotope[a]	CAS Registry Number	Natural abundance, %	Half-life, s
^{24}Si	[15759-98-5]		0.10
^{25}Si	[15759-89-4]		0.22
^{26}Si	[14932-60-6]		2.23
^{27}Si	[14276-59-6]		4.14
^{28}Si	[14276-58-5]	92.23	
^{29}Si	[14304-87-1]	4.67	
^{30}Si	[13981-69-6]	3.10	
^{31}Si	[14276-49-4]		2.62[b]
^{32}Si	[15092-72-5]		160[c]
^{33}Si	[34809-98-8]		6.1
^{34}Si	[29675-19-2]		2.8
^{35}Si	[34809-99-9]		0.9
^{36}Si	[34810-00-9]		0.5

[a] Also known are ^{22}Si, ^{37}Si, ^{38}Si, and ^{39}Si.
[b] Value shown is in hours.
[c] Value shown is in years.

Table 2. **Structure of Silicon**

Parameter	Value, at 101.3 kPa (1 atm)
crystal structure	diamond cubic
lattice spacing[a], pm	543.0[b]
atoms per unit cell	8
space group	F*d*3*m*
ionic radius[c], Si^{4+}, pm	42
Si–Si single bond length, pm	234

[a] Impurity atoms having an ionic radius greater than that of silicon cause lattice expansion.
[b] Value depends on crystal purity. For example, the presence of 0.1 atom % boron causes a lattice constriction of about 0.03%.
[c] Value is based on the Ahrens' calculation.

Table 3. **Isotropic and Anisotropic Silicon Properties**

Property	Tensor rank	Anisotropic
density	0	no
heat capacity	0	no
pyroelectric coefficient	1	yes
thermal expansion	2	no
thermal conductivity	2	no
electrical conductivity	2	no
electrical mobility	2	no
diffusion coefficient	2	no
piezoelectric coefficient	3	yes
elastic constants	4	yes
piezoresistance coefficient	4	yes
hardness		yes
breaking strength		yes
chemical etch rate[a]		yes
oxidation rate		yes
ion implant depth		yes
crystal growth rate		yes

[a] For some etchants.

Table 4. **Properties of Silicon**

Property	Value	Reference
density, at 25°C, g/cm^3	2.329	5
atomic density[a], atoms/cm^3	5×10^{22}	
hardness		6
Mohs'	6.5	
Knoop	950–1150	
elastic constants, GPa[b]		7
C_{11}	165.7	
C_{12}	63.9	
C_{44}	79.57	
Young's modulus in GPa[b]	170 ⟨110⟩ direction	8
bulk modulus[a], GPa[b]	100	
fracture stress, GPa[b]	2.8[c]	9
melting point, °C	1414	10
volume expansion on freezing, %	9.5	11
boiling point, °C	2355	10
debye temperature, K	645	12
critical temperature, °C	4886	13
critical volume, cm^3/mol	232.6	13
critical pressure, MPa[d]	53.6	13
heat of fusion, kJ/mol[e]	50.660	14
heat of vaporization, kJ/g[e]	16	13
vapor pressure, Pa[f]		15
800°C	1.33×10^{-8}	
1000°C	1.33×10^{-5}	
1500°C	2.66	
2000°C	80	

[a] Calculated value.

[b] To convert GPa to dyn/cm^2, multiply by 10^{10}.

[c] Average value.

[d] To convert MPa to atm, divide by 0.101.

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

[f] To convert Pa to mm Hg, multiply by 0.0075.

Table 5. **Properties of Liquid Silicon**[a]

Property	At mp	At 1500°C	Reference
thermal conductivity, W/(m·K)	41.84		13
dynamic viscosity, mPa·s(=cP)	0.88	0.7	13
kinematic viscosity, mm^2/s(=cST)	0.347[b]	0.28[b]	
surface tension, mN/m(=dyn/cm)	736	720	13
heat capacity, J/(kg·K)[c]	0.16	6.84	13
density, g/cm^3	2.533	2.50	13
electrical resistivity, $\mu\Omega$·cm	80	100	16
total optical emissivity	0.33	0.33	17
reflectivity at 633 nm, %	72	70	18

[a] Many of these values are extrapolated; see Ref. 19 for more details.
[b] Calculated value.
[c] To convert J to cal, divide by 4.184.

Table 6. **Equilibrium Segregation Coefficients for Impurities in Silicon**

Impurity[a]	k_e	Impurity[a]	k_e
Zn	$\sim 1 \times 10^{-5}$	Sb	2.3×10^{-2}
Cd	$\sim 1 \times 10^{-6}$	Bi	7×10^{-4}
B	8.0×10^{-1}	S	$\sim 1 \times 10^{-5}$
Al	2.0×10^{-3}		
Ga	8.0×10^{-3}	Cu	4×10^{-4}
In	4×10^{-4}	Au	2.5×10^{-5}
		Fe	8×10^{-6}
P	3.5×10^{-1}	O[b]	1.40
As	3×10^{-1}	C	7×10^{-2}

[a] Ref. 32.
[b] Values <1 have also been reported. Values of k_0 for oxygen in silicon are under extensive discussion.

Table 7. **Principal Producers of Silicon Alloys and/or Silicon Metal in the United States, 2004**[a]

Producer	Plant location	Product[b]
CC Metals and Alloys, Inc.	Calvert City, Ky.	FeSi
Elkem Metals Co.	Alloy, W.V.	FeSi and Si
Globe Metallurgical, Inc.[c]	Beverly, Ohio	FeSi and Si
	Selma, Ala.	Si
Oxbow Carbon and Minerals LLC[d]	Bridgeport, Ala.	FeSi
Simcala, Inc.	Mt. Meigs, Ala.	Si

[a] Ref. 38.
[b] FeSi, ferrosilicon (includes miscellaneous silicon alloys); Si, silicon metal.
[c] Globe's silicon ferroalloys plant located in Niagara Falls, N.Y., was idle in 2004.
[d] Formerly Applied Industrial Minerals Corp.

Table 8. **U.S. Silicon Statistics**[a,b]

Salient statistics	2001	2002	2003	2004	2005
production	282	261	253	275	276
imports for consumption	231	285	315	338	330
exports	23	22	26	24	23
consumption, apparent	502	540	544	595	577
price, average, cents per pounds Si:					
ferrosilicon, 50% Si	42.8	41.1	47.7	58.2	56
ferrosilicon, 75% Si	31.9	32.8	45.3	55.4	48
silicon metal	50.5	53.2	61.3	81.9	77
stocks, producer, yearend	40	25	22	16	22
net import reliance as a percentage of apparent consumption	44	52	54	54	52

[a] Ref. 39.

[b] Data in 10^3 t.