MANUFACTURE OF SEMI-CONDUCTOR GRADE SILICON*

V. RAMAKRISHNA

Chemistry Department, Indian Institute of Technology, New Delhi.

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Methods of manufacture of elemental *Si* are considered in the light of its occurrence and abundance in nature. The thermodynamics of the reactions involved in the manufacture and in the refining process has been discussed. Some commercial processes for obtaining semiconductor grade *Si* are outlined.

OCCURRENCE & ABUNDANCE

To be able to consider a method of producing an element on a large scale, it is useful to know in what form the element occurs and its abundance. *Si* has an atomic number of 14 (atomic weight = 28·1). Its electron iconfiguration is ($1s^2$, $2s^2$ $2p^6$, $3s^2$, $3p^2$) in the unexcited state. *Si* has three stable isotopes with mass numbers *28* (92·27%), *29* (4·68%) and *30* (3·05%). It is the second element in group IV (B) of the periodic table comparising *C*, *Ge*, *Si*, *Sn* and *Pb*. Its nearest neighbours in the periodic table are *Al*, *P*, *B* and Carbon. It is the second most abundant[1] element in the earth's crust—next only to oxygen (Table 1).

TABLE 1

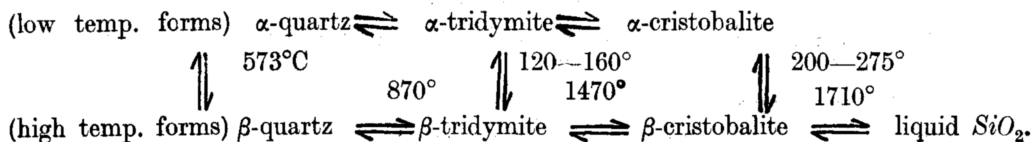
ABUNDANCE OF SOME ELEMENTS IN EARTH'S CRUST

Atomic No.	Element	Weight % in earth's crust	Atom % in earth's crust
1	H	1·00	17·25
6	C	0·35	0·50
7	N	0·04	0·05
8	O	49·13	53·2
13	Al	7·45	4·8
14	Si	26·00	16·0
15	P	0·12	0·07
16	S	0·10	0·05
22	Ti	0·61	0·20
24	Cr	0·03	0·008
26	Fe	4·20	1·25
29	Cu	0·01	0·003
32	Ge	4×10^{-4}	10^{-5}
33	As	5×10^{-4}	10^{-4}
47	Ag	1×10^{-5}	10^{-6}
78	Pt	2×10^{-5}	10^{-7}
79	Au	5×10^{-7}	10^{-7}
92	U	4×10^{-4}	10^{-5}

*Adopted from a lecture given to the Institute of Telecommunication Engineers, Delhi.

It is interesting to note that although *Si* is several times more abundant than most other common elements, elemental *Si* is much less familiar. Although *Si* holds the same position in the inorganic world as carbon in the organic, this fact has not been fully appreciated and exploited by inorganic chemists until recently.

Si does not exist as elemental *Si* in nature, but occurs extensively as its oxide, SiO_2, commonly known as quartz. Other forms of SiO_2 are tridymite and cristobalite.



All elements which show lithophile tendencies—like alkali and alkaline earth metals *Al* & *Fe*—form silicates which are a part of the crust of all igneous rocks, granite and basalt[2].

MANUFACTURE OF ELEMENTAL SILICON

Silicon oxide SiO_2 is the raw material. Table 2 gives the values[3] of the "standard heat" and "free energy of formation" in respect of some oxides including SiO_2. It is evident from these values that SiO_2 is a very stable oxide and that oxygen is firmly bound to silicon. In order to compare the relative stabilities of various oxides under the same conditions of temperature and oxygen potential, it is more convenient to use $\triangle G°$ values for the formation of the oxide at various temperatures based on *one mole* of oxygen rather than one mole of the oxide. This is shown graphically[4] in Fig 1. The oxide for which the graph occurs lower in Fig. 1 is the more stable under the same conditions of temperature and oxygen pressure i.e. oxygen will have a tendency to get transferred from an oxide occurring higher in Fig. 1 to an element whose oxide occurs lower. Thus *Al* or an alkaline earth or alkali metal can be used for the reduction of silica to elemental silicon. Alternatively, it will be observed from Fig. 1 that whereas *CO* is less stable than SiO_2 at lower temperatures, it becomes more stable at temperatures above 1,540°C so that carbon can be used for the reduction of SiO_2 to the elemental state. Thus the most common

TABLE 2

VALUES OF "STANDARD HEAT" AND "FREE ENERGY OF FORMATION" FOR SOME OXIDES

	SiO_2 (Crystobalite)	CO_2 (g)	CO (g)	H_2O (g)	Fe_2O_3 (s)	CuO	Al_2O_3
$\triangle H°$ 298 (Cals./mole)	—209,550	—94,052	—26,416	—57,800	—196,200	—38,300	—400,400
$\triangle H°$ 1500 (Cals./mole)	—207,350	—94,560	—27,540	—59,840	—191,500	—40,100	—402,700
$\triangle G°$ 298 (Cals./mole)	—196,600	—94,260	—32,810	—54,635	—176,800	—31,700	—378,100
$\triangle G°$ 1500 (Cals./mole)	—146,300	—94,710	—58,370	—39,260	—104,800	—5,400	—286,100

TABLE 3

FREE ENERGY CHANGE FOR REACTIONS, (1) TO (4)

Temperature (° Abs.)	REACTIONS (1)	(2)	(3)	(4)
	G°_{T} (cals.)			
1,000	70,920	—11,100	93,120	82,400
1,200	54,200	—10,800	75,800	66,500
1,400	37,680	—10,500	58,680	50,700
1,600	21,340	—10,100	41,540	34,600
1,800	4,340	—9,000	22,340	20,500
2,000	—13,220	—7,200	11,180	6,600
2,200	—30,280	—5,400	—19,480	—6,900

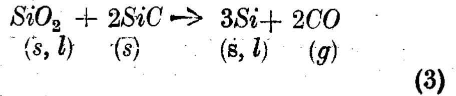
method employed for commercial production is the reduction of silica with carbon at high temperatures obtained in an electric arc furnace.

In addition to the reduction reaction

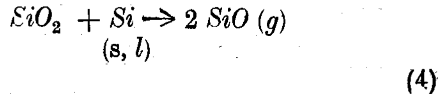
$$SiO_2 + 2C \rightarrow Si\ (l) + 2CO\ (g) \quad (1)$$

there are other side reactions which become important at these high temperatures namely

$$\underset{(s,\ l)}{Si} + C \rightarrow Si\,C\ (s) \quad (2)$$



$$\underset{(s,\ l)}{SiO_2} + \underset{(s)}{2SiC} \rightarrow \underset{(s,\ l)}{3Si} + \underset{(g)}{2CO} \quad (3)$$



$$SiO_2 + \underset{(s,\ l)}{Si} \rightarrow 2\ SiO\ (g) \quad (4)$$

Free energy changes[3] for reactions (1) to (4) are recorded in Table 3.

To suppress reaction (2), it is necessary to work at higher temperatures and not under too drastic reducing conditions i.e. excess of silica and not an excess of carbon should be present. Reaction (2) can also be suppressed by reducing the activity of Si, as for example by keeping it in solution in molten Fe— in which case the product will not

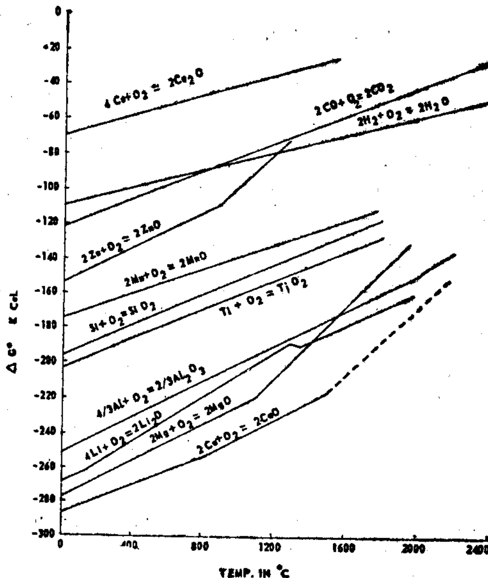


Fig .1—Free energy of formation of Oxides

be elemental Si but a solution of Si in Fe (known as ferrosilicon). It must also be observed that higher temperatures encourage reaction (4) to go in the forward direction, resulting in the loss of Si as $SiO(g)$. This gas undergoes disproportionation (reverse reaction) in the colder parts of the furnace and may cause a nuisance in its operation.

Thus, a judicious control of temperature and reducing conditions must be exercised to obtain elemental silicon in a smooth operation. Molten silicon is tapped off from the bottom of the furnace into copper moulds. The crude material has a purity of 93–98% and costs in U.S.A. approximately 18 cent per lb. The cost of silicon in a 50% ferrosilicon alloy is approximately 12 cents per lb. Si. The cost of semiconductor grade Si used to be $400 per lb.

PURIFICATION AND REFINING OF SILICON

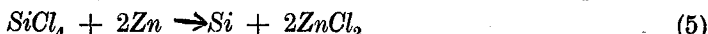
Various methods of purifying crude silicon have been developed and commercially exploited.

Tucker's process

The earliest method was that developed by Tucker[5]. He found that: "in commercial silicon the impurities are either in distinct strata or in the intercrystalline boundaries. When this material is attacked by acids, the impurities consisting mostly of iron and aluminum silicates and silicides of iron, calcium and magnesium, are dissolved. Evil-smelling and inflammable hydrides of silicon are evolved". If the best available commercial Si is finally powdered and treated successively with aqua regia, HF and H_2SO_4 acids and finally with HCl acid, a product is obtained which contains 99·94% Si. General Electric Company used this method for obtaining Si for microwave mixers.

Dupont's "Hyperpure Si" process

The Dupont process described by Lyon, *et al*[6] converts the crude silicon to $SiCl_4$ which is then reduced in the vapour phase with Zn vapour in a fused quartz apparatus :



$$SiCl_4 + 2Zn \rightarrow Si + 2ZnCl_2 \qquad (5)$$

The vapours of $SiCl_4$ and Zn are fed from a vaporiser maintained at 650°C into a reaction chamber maintained at 950°C. Normally a slight excess of $SiCl_4$ is present in the reactor. Si deposits as needles in the reactor. Unreacted $SiCl_4$ and Zn together with $ZnCl_2$ formed, pass through a tube at 1,000°C into a collector where Zn and $ZnCl_2$ are retained, $SiCl_4$ passing on to condensing system.

The product is removed from the chamber, crushed and treated with dilute HCl acid for 12 hours or more. It is then fumed with HF and H_2SO_4 acids, washed thoroughly and dried at 110°C. The metallic grey needles are then consolidated into massive silicon.

High temperature purification processes

Several high temperature purification processes are known to have been successfully applied. Scaff[7], for example, has purified 99·85% Si by heating it to a temperature above the melting point (1,600°C). The fused mass is then cooled at such a rate that solidification starts at one point, plane or zone, and proceeds in a slow orderly manner therefrom throughout the mass. The resulting silicon comprises zones having distinctly different electrical characteristics.

By far the most promising of these high temperature refining processes is the electron beam melting (e.b.m.) technique developed mainly by Temescal[8] and extensively applied ever since. This process combines the main advantages of vacuum induction melting

(ample time may be allowed for purifying reactions to take place) and consumable arc processes (contamination from container materials is avoided). In this process, a stream of electrons obtained usually from a heated filament, is accelerated by a high voltage electrostatic field and focused by means of electromagnetic lines on to the charge to be heated. Suitable shielding is provided for X-rays generated in this process. The applied accelerating voltage is usually of the order of 10,000 to 20,000 volts with a current of about 12 amps. The vacuum inside the chamber needs to be of the order of 10^{-5} torr. If the residual pressure is greater than 10^{-5} torr, glow discharges occur and in extreme cases even arc discharges. This may render the system unstable necessitating the halting of the operation.

By suitably arranging a "near ring cathode", it is possible to split the electron beam into two—one focused on the bottom of the consumable electrode and the other on to the surface of the ingot being built up inside a water cooled copper crucible. Because the focusing aspect of the beam is critical, it is normal to maintain the geometry of the system approximately constant by retracting the ingot and advancing the consumable electrode (Fig. 2). Sometimes two ring cathodes are used—one for focussing on to the bath and the other on to the electrode; or alternatively, the ring cathode is positioned farther away and a separate accelerating anode is used so that the molten material and the electrode do not act as anode.

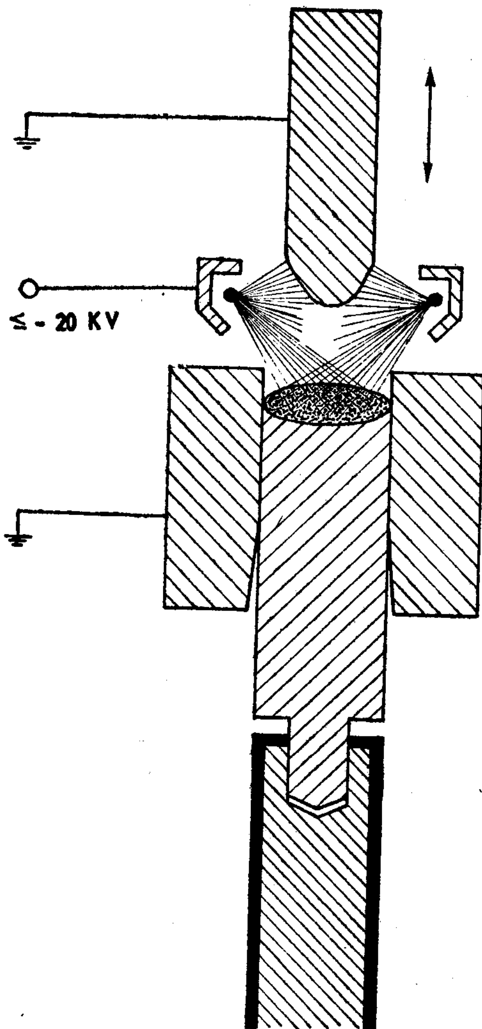


Fig. 2—Electron beam melting furnace (schematic)

Another technique developed by Heraeus[9] is to use an electron beam gun. This facilitates the use of higher pressures (10^{-3} torr) in the refineries chamber while keeping a low pressure (10^{-5} torr) in the electron gun chamber. Temscal[8] in U.S.A. and Degnassa & Heraeus in Europe manufactured electron beam furnaces of capacity 30, 240, 500 and 1,000 kW. Maximum size of the ingot was length 6 ft., dia. 20 in. The purification achieved by this process was variable but under suitable conditions it could be better than 99·99%.

The halide processes

These offer greater flexibility in operation and better removal of impurities at lower temperatures.

It will be observed from Fig. 3, which plots thermodynamic data ($\triangle G^{\circ}_T$) for the reactions of silicon tetrahalides as a function of temperature[10], that none of the tetrahalides decompose to the elements at near atmospheric pressure below the melting point

TABLE 4

DEGREE OF DISSOCIATION OF SOME IODIDES AT 123·5° ABS.

Iodide	Total pressure		
	10μ	250μ	500μ
BI_3	5·1%	1·7%	1·4%
PI_3	100%	100%	100%
AsI_3	100%	100%	100%
SbI_3	100%	100%	100%

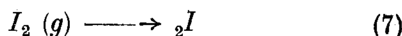
of Si (1,686° Abs), excepting perhaps SiI_4 for which the data are somewhat uncertain. Some recent data on the equilibrium constant for the reaction

$$Si\ (s) + 2I_2\ (g) \longrightarrow SiI_4\ (g) \qquad (6)$$

have shown that the spontaneous decomposition of the tetraiodide probably occurs[11] at 1,800° Abs.

The decomposition of the halides can, however, be increased by lowering the total pressure. Lot of literature has accumulated on the extent of decomposition (degree of dissociation) of SiI_4 and other possible impurity iodides as a function of pressure at various temperatures. Some values[12] obtained at 982°C (1,255° Abs.) are given in Table 4.

Table 4 does not take into account the degree of dissociation of I_2 itself or other replacement reactions. It is also apparent that the degree of dissociation of impurity iodides increases as the pressure is decreased from 500 μ to 10 μ. Thus it seems possible to deposit Si at temperatures between 770 and 1,200°C provided the pressure is kept sufficiently low. An interesting calculation would be the total pressure to be maintained for a 50 per cent dissociation of SiI_4, taking into account the dissociation of I_2 molecules :



$$I_2\ (g) \longrightarrow 2I \qquad (7)$$

At 1,000° Abs., the total pressure works out[10] to be 3·35 mm. In order to keep the pressure of I_2 (which is released as the product of decomposition) low, a simple arrangement of holding crude silicon in the decomposition bulb at 600-850°C serves extremely well. This indeed is the principle of the standard de Boer type deposition bulb.

Silicon tetraiodide seems to offer other advantages. For example it can be easily separated from other impurity iodides by fractional distillation at low pressures. Litton & Anderson[13] have studied the relative volatilities of various iodides at a pressure 200 torr, assuming that Raoult's law applies to this solution. This pressure corresponds to a boiling point of 238·1°C for SiI_4. Their data[13] recorded in Table 5 is of some interest.

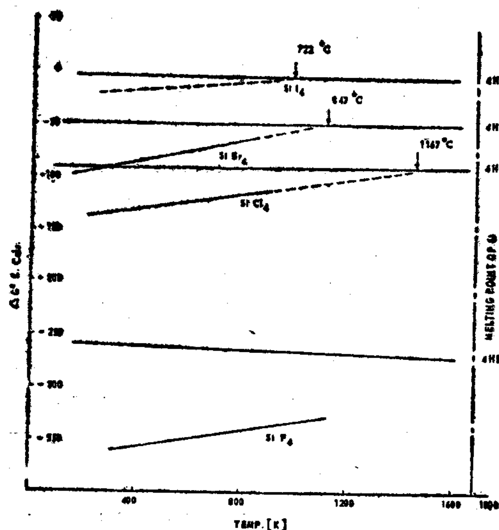


Fig. 3—Free energy of formation of Si and hydrogen halides.

TABLE 5

VOLATILITY OF GROUP III & V METAL IODIDES

Iodide	B.P. at 200 torr (°C)	Vapour pressure at 238°C (torr)	(Volatility) a
BI_3	157	1360	6·8
PI_3	169	910	4·6
GaI_3	299	36	0·18
Al_2I_6	324	24	0·12
AsI_3	336	24	0·12
SbI_3	369	11	0·06

Under the conditions specified in the Table, boron and phosphorus iodides are removed completely in the first fraction of the distillate, while the remaining tend to be left behind in the distillation vessel. These observations are particularly significant in view of the fact that if B were to remain as an impurity in Si, it cannot be separated by zone refining, as its distribution coeff. $K \simeq 0{\cdot}8$.

Litton & Anderson[13] studied the rate of silicon deposition (from thermal decomposition of SiI_4 on a heated filament) in a de Boer type deposition bulb made of inconel metal. The variables studied were (*i*) amount of I_2 in the cell; (*ii*) deposition bulb temperature (*iii*) observed filament temperature. Their results indicate that there is an optimum value of I_2 in the cell, beyond which the rate of deposition decreases for optimum range of bulb temperatures (425–475°C), while the rate goes on increasing with increasing filament temperature.

From Table 5, it will be apparent that the preparation of SiI_4 itself can be used as a purification stage. Rubin *et. al.*[14] purified the SiI_4 further by recrystallisation from toluene, followed by sublimation and finally by zone refining. The iodide thus obtained was stated to be suitable for decomposition to yield silicon for being used directly in semi-conductor devices.

Hydrogen reduction of silicon halides is another procedure investigated and adopted by Szekely[15]. Although the thermal decomposition of pure halides has not been found to be a feasible process (Fig. 3), their decomposition to yield the corresponding H-halides is certainly convenient. The lowest decomposition temperatures are determined by the intersection points in Fig. 2 of the Si-halide and H-halide lines. For example, for the iodide system the temperature is ~ 722°C, for the bromide system ~ 847°C and for the chloride system ~ 1,167°C. Szekely studied in detail the deposition of Si on a graphite cylinder from SiI_4 at 900–1,000°C. The variables studied were H_2 flow rate, reaction temperature, presence of a preheater and SiI_4 reservoir temperature. In a typical run as much as 55% of theoretical yields were obtained.

The consideration of the halide processes will not be complete without briefly mentioning what is otherwise come to be known as a "dihalide process". In this process the vapour of silicon tetrahalide is passed over silicon heated to 1100 to 1350°C and the lower halide

is formed. This is then allowed to undergo disproportionation at a lower temperature to yield Si and the higher halides[16]. According to a British patent on this process, better yields are obtained with silicon tetra-iodide. The equilibrium

$$Si + SiCl_4 \rightleftharpoons 2SiCl_2 \quad (8)$$

has been studied by Schafer and Nickl[17] and

$$Si + SiI_4 \rightleftharpoons 2SiI_2 \quad (9)$$

by Schafer & Morcher[18].

FINAL PURIFICATION OF SILICON

It is generally difficult to apply the original Pfann zone refining technique to silicon because of its tendency to react with the container material (quartz and graphite) at the temperatures involved. On a laboratory scale this difficulty has been overcome by eliminating the container completely as in the floating zone method developed by Keck[19]. However, impurities like boron (distribution coefficient 0·8) and phosphorus are removed with difficulty or not at all by this process and therefore have to be separated at some earlier stage. In the floating zone technique a bar of the element is held vertical in such a way that when the zone melts, the liquid will remain in place on account of its own surface tension. A detailed description of a laboratory scale apparatus has been described by Winegard *et. al.*[20]

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