

																1	2																														
																H	He																														
3	4																	5	6	7	8	9	10																								
Li	Be																	B	C	N	O	F	Ne																								
11	12																	13	14	15	16	17	18																								
Na	Mg																	Al	Si	P	S	Cl	Ar																								
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																														
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																														
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																														
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72																														
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																														
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104																														
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uub																																					
																		105	106	107	108	109	110	111	112																						
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# 9

## Silicon

### 9.1 Introduction

Silicon shows a rich variety of chemical properties and it lies at the heart of much modern technology.<sup>(1)</sup> Indeed, it ranges from such bulk commodities as concrete, clays and ceramics, through more chemically modified systems such as soluble silicates, glasses and glazes to the recent industries based on silicone polymers and solid-state electronics devices. The refined technology of ultrapure silicon itself is perhaps the most elegant example of the close relation between chemistry and solid-state physics and has led to numerous developments such as the transistor, printed circuits and microelectronics (p. 332).

In its chemistry, silicon is clearly a member of Group 14 of the periodic classification but there are notable differences from carbon, on the one hand, and the heavier metals of the group on the other (p. 371). Perhaps the most

obvious questions to be considered are why the vast covalent chemistry of carbon and its organic compounds finds such pallid reflection in the chemistry of silicon, and why the intricate and complex structural chemistry of the mineral silicates is not mirrored in the chemistry of carbon-oxygen compounds.<sup>†</sup>

Silica (SiO<sub>2</sub>) and silicates have been intimately connected with the evolution of mankind from prehistoric times: the names derive from the Latin *silex*, gen. *silicis*, flint, and serve as a reminder of the simple tools developed in paleolithic times (~500 000 years ago) and the shaped flint knives and arrowheads of the neolithic age which began some 20 000 years ago. The name of the element, silicon, was proposed by Thomas Thomson in

<sup>†</sup> Throughout this chapter we will notice important differences between the chemical behaviour of carbon and silicon, and one is reminded of Grant Urry's memorable words: "It is perhaps appropriate to chide the polysilane chemist for milking the horse and riding the cow in attempting to adapt the success of organic chemistry in the study of polysilanes. A valid argument can be made for the point of view that the most effective chemistry of silicon arises from the differences with the chemistry of carbon compounds rather than the similarities" (see ref. 35 on p. 342).

<sup>1</sup> *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd edn., Vol. 20, pp. 748-973 (1982) (Silica, silicon and silicon alloys; Silicon compounds); 4th edn., Vol. 5 (1993) Cement pp. 564-98; Ceramics, pp. 599-697; Ceramics as electrical materials, pp. 698-728; Clays, Vol. 6, pp. 381-423 (1993).

1831, the ending *on* being intended to stress the analogy with carbon and boron.

The great affinity of silicon for oxygen delayed its isolation as the free element until 1823 when J. J. Berzelius succeeded in reducing  $K_2SiF_6$  with molten potassium. He first made  $SiCl_4$  in the same year,  $SiF_4$  having previously been made in 1771 by C. W. Scheele who dissolved  $SiO_2$  in hydrofluoric acid. The first volatile hydrides were discovered by F. Wöhler who synthesized  $SiHCl_3$  in 1857 and  $SiH_4$  in 1858, but major advances in the chemistry of the silanes awaited the work of A. Stock during the first third of the twentieth century. Likewise, the first organosilicon compound  $SiEt_4$  was synthesized by C. Friedel and J. M. Crafts in 1863, but the extensive development of the field was due to F. S. Kipping in the first decades of this century.<sup>(2)</sup> The unique properties and industrial potential of siloxanes escaped attention at that time and the dramatic development of silicone polymers, elastomers, and resins has occurred during the past 50 years (p. 365).

The solid-state chemistry of silicon has shown similar phases. The bizarre compositions derived by analytical chemistry for the silicates only became intelligible following the pioneering X-ray structural work of W. L. Bragg in the 1920s<sup>(3)</sup> and the concurrent development of the principles of crystal chemistry by L. Pauling<sup>(4)</sup> and of geochemistry by V. M. Goldschmidt.<sup>(5)</sup> More recently the complex crystal chemistry of the silicides has been elucidated and the solid-state chemistry of doped semiconductors has been developed to a level of sophistication that was undreamt of even in the 1960s.

<sup>2</sup> E. G. ROCHOW, Silicon, Chap. 15 in *Comprehensive Inorganic Chemistry*, Vol. 1, pp. 1323–467, Pergamon Press, Oxford, 1973. See also E. G. ROCHOW, *Silicon and Silicones*, Springer-Verlag, Newark, N.J., 1987, 181 pp.

<sup>3</sup> W. L. BRAGG, *The Atomic Structure of Minerals*, Oxford University Press, 1937, 292 pp.

<sup>4</sup> L. PAULING, *The Nature of the Chemical Bond*, 3rd edn., pp. 543–62, Cornell University Press, 1960, and references cited therein.

<sup>5</sup> V. M. GOLDSCHMIDT, *Trans. Faraday Soc.* **25**, 253–83 (1929); *Geochemistry*, Oxford University Press, Oxford, 1954, 730 pp.

## 9.2 Silicon

### 9.2.1 Occurrence and distribution

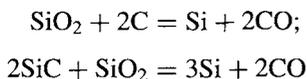
Silicon (27.2 wt%) is the most abundant element in the earth's crust after oxygen (45.5%), and together these 2 elements comprise 4 out of every 5 atoms available near the surface of the globe. This implies that there has been a substantial fractionation of the elements during the formation of the solar system since, in the universe as a whole, silicon is only seventh in order of abundance after H, He, C, N, O and Ne (p. 4). Further fractionation must have occurred within the earth itself: the core, which has 31.5% of the earth's mass, is commonly considered to have a composition close to  $Fe_{25}Ni_2Co_{0.1}S_3$ ; the mantle (68.1% of the mass) probably consists of dense oxides and silicates such as olivine  $(Mg,Fe)_2SiO_4$ , whereas the crust (0.4% of the mass) accumulates the lighter siliceous minerals which "float" to the surface. The crystallization of igneous rocks from magma (molten rock, e.g. lava) depends on several factors such as the overall composition, the lattice energy, mp and crystalline complexity of individual minerals, the rate of cooling, etc. This has been summarized by N. L. Bowen in a reaction series which gives the approximate sequence of appearance of crystalline minerals as the magma is cooled: olivine  $[M_2^{II}SiO_4]$ , pyroxene  $[M_2^{II}Si_2O_6]$ , amphibole  $[M_7^{II}\{(Al,Si)_4O_{11}\}(OH)_2]$ , biotite mica  $[(K,H)_2(Mg,Fe)_2(Al,Fe)_2(SiO_4)_3]$ , orthoclase feldspar  $[KAlSi_3O_8]$ , muscovite mica  $[KAl_2(AlSi_3O_{10})(OH)_2]$ , quartz  $[SiO_2]$ , zeolites and hydrothermal minerals. The structure of these mineral types is discussed later (p. 347), but it is clear that the reaction series leads to progressively more complex silicate structural units and that the later part of the series is characterized by the introduction of OH (and F) into the structures. Extensive isomorphous substitution among the metals is also possible. Subsequent weathering, transport and deposition leads to sedimentary rocks such as clays, shales and sandstones. Metamorphism at high temperatures and pressures can effect further

changes during which the presence or absence of water plays a vital role.<sup>(6,7)</sup>

Silicon never occurs free: it invariably occurs combined with oxygen and, with trivial exceptions, is always 4-coordinate in nature. The {SiO<sub>4</sub>} unit may occur as an individual group or be linked into chains, ribbons, rings, sheets or three-dimensional frameworks (pp. 347–59).

### 9.2.2 Isolation, production and industrial uses

Silicon (96–99% pure) is now invariably made by the reduction of quartzite or sand with high purity coke in an electric arc furnace; the SiO<sub>2</sub> is kept in excess to prevent the accumulation of SiC (p. 334):



The reaction is frequently carried out in the presence of scrap iron (with low P and S content) to produce ferrosilicon alloys: these are used in the metallurgical industry to deoxidize steel, to manufacture high-Si corrosion-resistant Fe, and Si/steel laminations for electric motors. The scale of operations can be gauged from the 1980 world production figures which were in excess of 5 megatonnes. Consumption of high purity (semiconductor grade) Si leapt from less than 10 tonnes in 1955 to 2800 tonnes in 1980.

Silicon for the chemical industry is usually purified to ~98.5% by leaching the powdered 96–97% material with water. Very pure Si for semiconductor applications is obtained either from SiCl<sub>4</sub> (made from the chlorination of scrap Si) or from SiHCl<sub>3</sub> (a byproduct of the silicone industry, p. 338). These volatile compounds are

purified by exhaustive fractional distillation and then reduced with exceedingly pure Zn or Mg; the resulting spongy Si is melted, grown into cylindrical single crystals, and then purified by zone refining. Alternative routes are the thermal decomposition of SiL<sub>4</sub>/H<sub>2</sub> on a hot tungsten filament (cf. boron, p. 140), or the epitaxial growth of a single-crystal layer by thermal decomposition of SiH<sub>4</sub>. A one-step process has also been developed to produce high-purity Si for solar cells at one-tenth of the cost of rival methods. In this process Na<sub>2</sub>SiF<sub>6</sub> (which is a plentiful waste product from the phosphate fertilizer industry) is reduced by metallic Na; the reaction is highly exothermic and is self-sustaining without the need for external fuel.

Hyperfine Si is one of the purest materials ever made on an industrial scale: the production of transistors (p. 332) requires the routine preparation of crystals with impurity levels below 1 atom in 10<sup>10</sup>, and levels below 1 atom in 10<sup>12</sup> can be attained in special cases.

### 9.2.3 Atomic and physical properties

Silicon consists predominantly of <sup>28</sup>Si (92.23%) together with 4.67% <sup>29</sup>Si and 3.10% <sup>30</sup>Si. No other isotopes are stable. The <sup>29</sup>Si isotope (like the proton) has a nuclear spin  $I = \frac{1}{2}$ , and is being increasingly used in nmr spectroscopy.<sup>(8)</sup> <sup>31</sup>Si, formed by neutron irradiation of <sup>30</sup>Si, has  $t_{\frac{1}{2}}$  2.62 h; it can be detected by its characteristic β<sup>-</sup> activity ( $E_{\text{max}}$  1.48 MeV) and is very useful for the quantitative analysis of Si by neutron activation. The radioisotope with the longest half-life (~172 y) is the soft β<sup>-</sup> emitter <sup>32</sup>Si ( $E_{\text{max}}$  0.2 MeV).

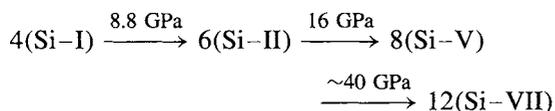
In its ground state, the free atom Si has the electronic configuration [Ne]3s<sup>2</sup>3p<sup>2</sup>. Ionization energies and other properties are compared with those of the other members of Group 14 on p. 372. Silicon crystallizes in the diamond

<sup>6</sup> B. MASON, *Principles of Geochemistry*, 3rd edn., Wiley, New York, 1966, 329 pp. P. HENDERSON, *Inorganic Geochemistry*, Pergamon Press, Oxford, 1982, 372 pp. S. R. ASTON (ed.), *Silicon Geochemistry and Biogeochemistry*, Academic Press, 1983, 272 pp.

<sup>7</sup> D. K. BAILEY and R. MACDONALD (eds.), *The Evolution of the Crystalline Rocks*, Academic Press, London, 1976, 484 pp.

<sup>8</sup> J.-P. KINTZINGER and H. MARSMANN, *Oxygen-17 and Silicon-29 NMR*, Vol. 17 of *NMR Basic Principles and Progress* (P. DIEHL, E. FLUCK and R. KOSFIELD, eds.), Springer-Verlag, Berlin, 1980, 250 pp.

lattice (p. 275) with  $a_0$  543.10204 pm at 25°, corresponding to an Si–Si distance of 235.17 pm and a covalent atomic radius of 117.59 pm. The density and lattice constant of pure single-crystal Si are now known sufficiently accurately to give a direct value of the Avogadro constant ( $N_A = 6.022\,1363 \times 10^{23} \text{ mol}^{-1}$ ) which is as precise as the best currently accepted value ( $6.022\,1367 \times 10^{23} \text{ mol}^{-1}$ ).<sup>(9)</sup> There appear to be no allotropes of Si at ambient pressure but the 4-coordinate diamond lattice of Si–I transforms to several other modifications at higher pressures, of which distorted-diamond Si–II, primitive hexagonal Si–V and eventually hexagonal close packed Si–VII may be mentioned; the structural sequence corresponds to a systematic increase in coordination number:<sup>(10)</sup>



[1 GPa = 10 kbar  $\approx$  9869 atm.]

Physical properties are summarized in Table 9.1 (see also p. 373). Silicon is notably more volatile than C and has a substantially lower energy of vaporization, thus reflecting the smaller

**Table 9.1** Some physical properties of silicon

MP/°C	1420
BP/°C	$\sim 3280$
Density (20°C)/g cm <sup>-3</sup>	2.53259
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$	$50.6 \pm 1.7$
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$	$383 \pm 10$
$\Delta H_f$ (monatomic gas)/kJ mol <sup>-1</sup>	$454 \pm 12$
$a_0/\text{pm}$	543.10204
$r$ (covalent)/pm	117.59
$r$ ("ionic")/pm	26 <sup>(a)</sup>
Pauling electronegativity	1.8

<sup>(a)</sup> This is the "effective ionic radius" for 4-coordinate Si<sup>IV</sup> in silicates, obtained by subtracting  $r(\text{O}^{II}) = 140$  pm from the observed Si–O distance. The value for 6-coordinate Si<sup>IV</sup> is 40 pm. [R. D. Shannon, *Acta Cryst.* **A32**, 751–67 (1976).]

<sup>9</sup> P. SEYFRIED and 13 others, *Z. Phys. B-Condensed Matter* **87**, 289–98 (1992).

<sup>10</sup> H. OLJNYK, S. K. SIKKA and W. B. HOLZAPFEL, *Phys. Lett.* **103A**, 137–40 (1984).

Si–Si bond energy. The element is a semiconductor with a distinct shiny, blue–grey metallic lustre; the resistivity decreases with increase of temperature, as expected for a semiconductor. The actual value of the resistivity depends markedly on purity but is  $\sim 40$  ohm cm at 25° for very pure material.

The immense importance of Si in transistor technology stems from the chance discovery of the effect in Ge at Bell Telephone Laboratories, New Jersey, in 1947, and the brilliant theoretical and practical development of the device by J. Bardeen, W. H. Brattain and W. Shockley for which they were awarded the 1956 Nobel Prize for Physics. A brief description of the physics and chemistry underlying transistor action in Si is given in the Panel (p. 332).

## 9.2.4 Chemical properties

Silicon in the massive, crystalline form is relatively unreactive except at high temperatures. Oxygen, water and steam all have little effect probably because of the formation of a very thin, continuous, protective surface layer of SiO<sub>2</sub> a few atoms thick (cf. Al, p. 224). Oxidation in air is not measurable below 900°; between 950° and 1160° the rate of formation of vitreous SiO<sub>2</sub> rapidly increases and at 1400° the N<sub>2</sub> in the air also reacts to give SiN and Si<sub>3</sub>N<sub>4</sub>. Sulfur vapour reacts at 600° and P vapour at 1000°. Silicon is also unreactive towards aqueous acids, though the aggressive mixture of conc HNO<sub>3</sub>/HF oxidizes and fluorinates the element. Silicon dissolves readily in hot aqueous alkali due to reactions of the type  $\text{Si} + 4\text{OH}^- = \text{SiO}_4^{4-} + 2\text{H}_2$ . Likewise, the thin film of SiO<sub>2</sub> is no barrier to attack by halogens, F<sub>2</sub> reacting vigorously at room temperature, Cl<sub>2</sub> at  $\sim 300^\circ$ , and Br<sub>2</sub>, I<sub>2</sub> at  $\sim 500^\circ$ . Even alkyl halides will react at elevated temperatures and, in the presence of Cu catalysts, this constitutes the preferred "direct" synthesis of organosilicon chlorides for the manufacture of silicones (p. 364).

In contrast to the relative inertness of solid Si to gaseous and liquid reagents, molten Si is an extremely reactive material: it forms alloys or

## The Physics and Chemistry of Transistors

In ultrapure semiconductor grade Si there is an energy gap  $E_g$  between the highest occupied energy levels (the valence band) and the lowest unoccupied energy levels (the conduction band). This is shown diagrammatically in Fig. a: the valence band is completely filled, the conduction band is empty, the Fermi level ( $E_F$ ), which is the energy at which the chance of a state being occupied by an electron is  $\frac{1}{2}$ , lies approximately midway between these, and the material is an insulator at room temperature. If the Si is doped with a Group 15 element such as P, As or Sb, each atom of dopant introduces a supernumerary electron and the impurity levels can act as a source of electrons which can be thermally or photolytically excited into the conduction band (Fig. b): the material is an n-type semiconductor with an activation energy  $\Delta E_n$  (where n indicates negative current carriers, i.e. electrons). Conversely, doping with a Group 13 element such as B, Al or Ga introduces acceptor levels that can act as traps for electrons excited from the filled valence band (Fig. c): the material is a p-type semiconductor and the current is carried by the positive holes in the valence band.

When an n-type sample of Si is joined to a p-type sample, a p-n junction is formed having a common Fermi level as in Fig. d: electrons will flow from n to p and holes from p to n thereby producing a voltage drop  $V_0$  across the space charge region. A p-n junction can thus act as a diode for rectifying alternating current, the current passing more easily in one direction than the other. In practise a large p-n junction might cover  $10\text{ mm}^2$ , whereas in integrated circuits such a device might cover no more than  $10^{-4}\text{ mm}^2$  (i.e. a square of side  $10\text{ }\mu\text{m}$ ).

A transistor, or n-p-n junction, is built up of two n-type regions of Si separated by a thin layer of weakly p-type (Fig. e). When the emitter is biased by a small voltage in the forward direction and the collector by a larger voltage in the reverse direction, this device acts as a triode amplifier. The relevant energy level diagram is shown schematically in Fig. f.

The large-scale reproducible manufacture of minute, electronically-stable, single-crystal transistor junctions is a triumph of the elegant techniques of solid-state chemical synthesis. The sequence of steps is illustrated in diagrams (i)-(v).

- (i) A small wafer of single-crystal n-type Si is oxidized by heating it in  $\text{O}_2$  or  $\text{H}_2\text{O}$  vapour to form a thin surface layer of  $\text{SiO}_2$ .
- (ii) The oxide coating is covered by a photosensitive film called "photoresist".
- (iii) A mask is placed over the photoresist to confine the exposure to the desired pattern and the chip is exposed to ultraviolet light; the exposed photoresist is then removed by treatment with acid, leaving a tough protective layer over the parts of the oxide coating that are to be retained.
- (iv) The unprotected areas of Si are etched away with hydrofluoric acid and the remaining photoresist is also removed.
- (v) The surface is exposed to the vapour of a Group 13 element and the impurity atoms diffuse into the unprotected area to form a layer of p-type Si.
- (vi) Steps (i)-(v) are repeated, with a different mask, and then the newly exposed areas are treated with the vapour of a Group 15 element to produce a patterned layer of n-type Si.
- (vii) Finally, again with a different mask, the surface is reoxidized and then re-etched to produce openings into which metal is deposited so as to connect the n- and p-regions into an integrated circuit.

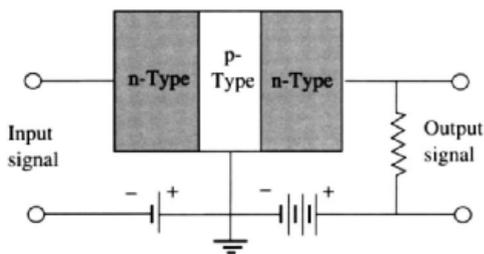
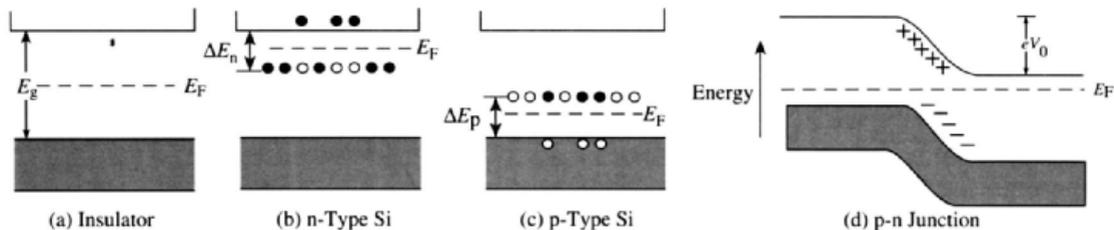
Each individual p-n diode or n-p-n transistor can be made almost unbelievably minute by these techniques; for example computer memory units storing over  $10^5$  bits of information on a single small chip are routinely used. Further information can be obtained from textbooks of solid-state physics or electronic engineering.

silicides with most metals (see below) and rapidly reduces most metal oxides because of the very large heat of formation of  $\text{SiO}_2$  ( $\sim 900\text{ kJ mol}^{-1}$ ). This presents problems of containment when working with molten Si, and crucibles must be made of refractories such as  $\text{ZrO}_2$  or the borides of transition metals in Groups 4-6 (p. 146).

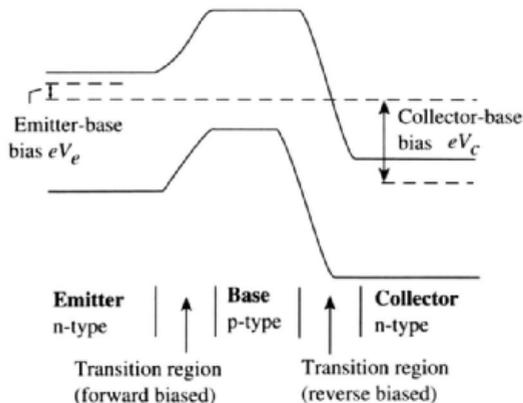
Chemical trends within Group 14 are discussed on p. 373. Silicon does not form binary compounds with the heavier members of the group (Ge, Sn, Pb) but its compound with carbon, SiC,

is of outstanding academic and practical interest, and is manufactured on a huge scale industrially (see Panel on p. 334).

In the vast majority of its compounds Si is tetrahedrally coordinated but sixfold coordination also occurs, and occasional examples of other coordination geometries are known as indicated in Table 9.2 (p. 335). Unstable 2-coordinate Si has been known for many years but in 1994 the stable, colourless, crystalline silylene  $[\text{:SiNBu}^t\text{CH}=\text{CHNBu}^t]$ , structure (1), p. 336, was

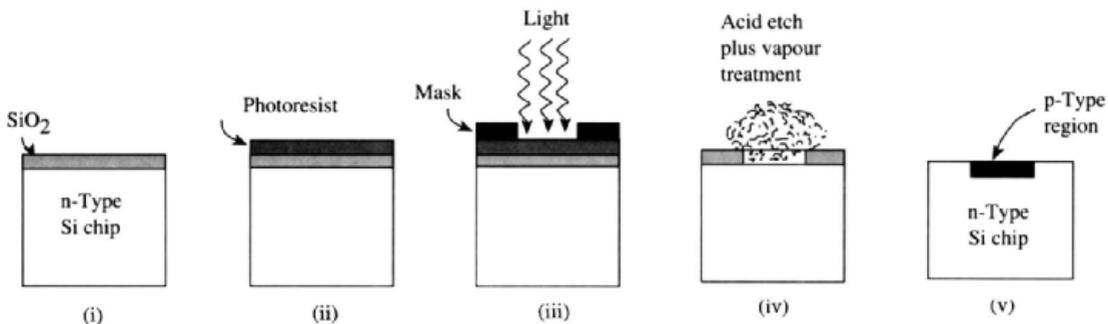


(e) An n-p-n transistor junction with the left n-p junction forward biased and the right p-n junction reverse biased



(f) Energy level diagram

Figs. (a)-(f) mentioned in Panel opposite.



Steps (i)-(v) mentioned in Panel opposite.

### Silicon Carbide, SiC<sup>(11,12)</sup>

Silicon carbide was made accidentally by E. G. Acheson in 1891; he recognized its abrasive power and coined the name "carborundum" from carbo(n) and (co)rundum (Al<sub>2</sub>O<sub>3</sub>) to indicate that its hardness on the Mohs scale (9.5) was intermediate between that of diamond (10) and Al<sub>2</sub>O<sub>3</sub> (9). Within months he had formed the Carborundum Co. for its manufacture, and current world production approaches 1 million tonnes annually.

Despite its simple formula, SiC exists in at least 200 crystalline modifications based on hexagonal  $\alpha$ -SiC (wurtzite-type ZnS, p. 1210) or cubic  $\beta$ -SiC (diamond or zincblende-type, p. 1210). The complexity arises from the numerous stacking sequences of the *a* and *b* "layers" in the crystal.<sup>(13)</sup> The  $\alpha$ -form is marginally the more stable thermodynamically. Industrially,  $\alpha$ -SiC is obtained as black, dark green or purplish iridescent crystals by reducing high-grade quartz sand with a slight excess of coke or anthracite in an electric furnace at 2000–2500°C:



The dark colour is caused by impurities such as iron, and the iridescence is due to a very thin layer of SiO<sub>2</sub> formed by surface oxidation. Purer samples are pale yellow or colourless. Even higher temperatures (and vacuum conditions) are required to produce the  $\beta$ -form. Alternatively, very pure  $\beta$ -SiC can be obtained by heating grains of ultrapure Si with graphite at 1500° or by gas-phase plasma decomposition of Me<sub>2</sub>SiCl<sub>2</sub>, MeSiCl<sub>3</sub> or SiCl<sub>4</sub>/CH<sub>4</sub> mixtures. Fibres of SiC are made by the progressive pyrolysis of organosilicon polymers such as -CH<sub>2</sub>SiHMe- or -CH<sub>2</sub>SiMe<sub>2</sub>-. Lattice constants for  $\alpha$ -SiC are *a* 307.39 pm, *c* 1006.1 pm, *c/a* 3.273; for cubic  $\beta$ -SiC, *a*<sub>0</sub> 435.02 pm (cf. diamond 356.68, Si 543.10, mean 449.89 pm).

SiC has greater thermal stability than any other binary compound of Si and decomposition by loss of Si only becomes appreciable at ~2700°. It resists attack by most aqueous acids (including HF but not H<sub>3</sub>PO<sub>4</sub>) and is oxidized in air only above 1000° because of the protective layer of SiO<sub>2</sub>; this can be removed by molten hydroxides or carbonates and oxidation is much more rapid under these conditions, e.g.:



Cl<sub>2</sub> attacks SiC vigorously, yielding SiCl<sub>4</sub> + C at 100° and SiCl<sub>4</sub> + CCl<sub>4</sub> at 1000°.

Technical interest in SiC originally stemmed from its excellence as an abrasive powder; this derives not only from the great intrinsic hardness of the compound but also from its peculiar fracture to give sharp cutting edges. As a refractory,  $\alpha$ -SiC combines great strength and chemical stability, with an extremely low thermal expansion coefficient ( $\sim 6 \times 10^{-6}$ ) which shows no sudden discontinuities due to phase transitions. Pure  $\alpha$ -SiC is an intrinsic semiconductor with an energy band gap sufficiently large ( $1.90 \pm 0.10$  eV) to make it a very poor electrical conductor ( $\sim 10^{-13}$  ohm<sup>-1</sup> cm<sup>-1</sup>). However, the presence of controlled amounts of impurities makes it a valuable extrinsic semiconductor ( $10^{-2} - 3$  ohm<sup>-1</sup> cm<sup>-1</sup>) with a positive temperature coefficient. This, combined with its mechanical and chemical stability, accounts for its extensive use in electrical heating elements. In recent years pure  $\beta$ -SiC has received much attention as a high-temperature semiconductor with applications in transistors, diode rectifiers, electroluminescent diodes, etc. (see p. 332). In fact, these various electrical and refractory uses account for only about 2% of the vast tonnages of SiC manufactured each year. About 43% is still used for its original application as an abrasive, and the remaining 55% is used in metallurgical processes, especially as a refining agent in the casting of iron and steel: the SiC reacts with free oxygen and with metal oxides to form CO and a siliceous slag.

isolated;<sup>(14)</sup> it distils without change at 85°C/0.1 torr and can be kept in solution in a sealed tube for several months at 150°C without

apparent change. A recent example of pyramidal 3-coordinate Si is the Si<sub>4</sub><sup>4-</sup> anion (isoelectronic with the tetrahedral P<sub>4</sub> molecule, p. 479), which has been shown to occur in the long-known red silicide CsSi.<sup>(17)</sup> There has been much discussion about the possibility of planar 4-coordinate Si in orthosilicate esters of pyrocatechol (2) but this is

<sup>11</sup> Kirk-Othmer *Encyclopedia of Chemical Technology*, 4th edn., Vol. 4, Silicon Carbide, 1992, pp. 891–911.

<sup>12</sup> *Silicon Carbide*, World Business Publications, Ltd., 2nd edn., 1988, 340 pp.

<sup>13</sup> *Gmelin Handbook of Inorganic Chemistry*, 8th edn., Springer-Verlag, Berlin, *Silicon Suppl. B2*, 1984, 312 pp. See also *Suppl. B1*, 1986, 545 pp. for further information on occurrence of SiC in nature, its manufacture, chemical reactions, applications, etc.

<sup>14</sup> M. DENK and 8 others, *J. Am. Chem. Soc.* **116**, 2691–2 (1994).

<sup>15</sup> T. J. BARTON and G. T. BURNS, *J. Am. Chem. Soc.* **100**, 5246 (1978).

<sup>16</sup> C. L. KREIL, O. L. CHAPMAN, G. T. BURNS and T. J. BARTON, *J. Am. Chem. Soc.* **102**, 841–2 (1980).

<sup>17</sup> G. KLICHE, M. SCHWARZ and H. G. VON SCHNERING, *Angew. Chem. Int. Edn. Engl.* **26**, 349–51 (1987).

Table 9.2 Coordination geometries of silicon

Coordination number	Examples
2 (bent)	SiF <sub>2</sub> (g), SiMe <sub>2</sub> (matrix, 77 K), [ $\overline{\text{SiNBu}^+\text{CH}=\text{CHNBu}^+}$ ] (1) <sup>(14)</sup>
3 (planar)	Silabenzene, SiC <sub>5</sub> H <sub>6</sub> , <sup>(15)</sup> silatoluene, C <sub>5</sub> H <sub>5</sub> SiMe <sup>(16)</sup>
3 (pyramidal)	Si <sub>4</sub> <sup>4-</sup> , (?)SiH <sub>3</sub> <sup>-</sup> in KSiH <sub>3</sub> (NaCl structure)
4 (tetrahedral)	SiH <sub>4</sub> , SiX <sub>4</sub> , SiX <sub>n</sub> Y <sub>4-n</sub> , SiO <sub>2</sub> , silicates, etc.
4 (planar)	(see text) <sup>(18)</sup> (2)
4 (see-saw, C <sub>2v</sub> )	SiLi <sub>4</sub> (3) <sup>(19)</sup>
5 (trigonal bipyramidal)	SiX <sub>5</sub> <sup>-</sup> , cyclo-[Me <sub>2</sub> NSiH <sub>3</sub> ] <sub>5</sub> , [Si(O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> (OPPh <sub>3</sub> )] (4) <sup>(20)</sup>
5 (square pyramidal)	[Si(O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> {OP(NC <sub>5</sub> H <sub>10</sub> )}] (5), <sup>(20)</sup> [SiF(O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> ] <sup>(21)</sup>
6 (octahedral)	SiF <sub>6</sub> <sup>2-</sup> , [Si(acac) <sub>3</sub> ] <sup>+</sup> , [L <sub>2</sub> SiX <sub>4</sub> ], SiO <sub>2</sub> (stishovite), SiP <sub>2</sub> O
7 (capped trig. antiprism)	[(2-(Me <sub>2</sub> NCH <sub>2</sub> )C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiH] (6) <sup>(22)</sup>
8 (cubic)	Mg <sub>2</sub> Si (antifluorite)
9 (capped square antiprism)	[μ <sub>8</sub> -SiCo <sub>9</sub> (CO) <sub>21</sub> ] <sup>2-</sup> (7) <sup>(23)</sup>
10 (various)	TiSi <sub>2</sub> , CrSi <sub>2</sub> , MoSi <sub>2</sub> , <sup>(24)</sup> [Si(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> ] (8) <sup>(25)</sup>

still far from being unequivocally established.<sup>(18)</sup> However, a 'one-sided' C<sub>2v</sub> geometry for SiLi<sub>4</sub> (3) seems probable.<sup>(19)</sup> Five-coordinate Si can be either trigonal bipyramidal or square pyramidal, e.g. (4), (5), etc.<sup>(20,21)</sup> Numerous examples of octahedral 6-coordination are known. A single example of 7-coordinate Si has been identified, (6)<sup>(22)</sup> and there are occasional examples of higher coordination numbers. Thus, Si has cubic 8-fold coordination in Mg<sub>2</sub>Si which has the antifluorite structure, Si occupying the Ca sites and Mg the F sites of the fluorite lattice (p. 118). The capped square antiprismatic structure of the anion [SiCo<sub>9</sub>(CO)<sub>21</sub>]<sup>2-</sup> has essentially 9-fold coordination about the encapsulated Si atom (7), with Si-Co<sub>base</sub> 231 pm, Si-Co<sub>upper</sub> 228 pm and Si-Co<sub>cap</sub> 252.7 pm; each of the four basal Co atoms has two terminal CO ligands, each of the

other five Co atoms has one, and there are eight bridging CO groups.<sup>(23)</sup> The coordination number 10 is found in the structures of several transition metal silicides<sup>(24)</sup> and in decamethylsilicocene (8). The crystal structure of this latter compound reveals two types of molecular geometry; one-third of the molecules have the two rings parallel and staggered as in [Fe(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] with Si-C 242 pm whereas the other two-thirds have non-parallel rings, implying a stereochemically active lone pair of electrons on the Si atom.<sup>(25)</sup> The bent (C<sub>s</sub>) structure persists in the gas phase, the angle between the two C<sub>5</sub> planes being 22°.

## 9.3 Compounds

### 9.3.1 Silicides<sup>(26,27)</sup>

As with borides (p. 145) and carbides (p. 297) the formulae of metal silicides cannot be rationalized by the application of simple valency rules, and

<sup>18</sup> W. HÖNLE, U. DETTLAUF-WEGLIKOWSKA, L. WALZ and H. G. VON SCHNERING, *Angew. Chem. Int. Edn. Engl.* **28**, 623-4 (1989), and references cited therein.

<sup>19</sup> P. VON RAGUÉ SCHLEYER and A. E. REED, *J. Am. Chem. Soc.* **110**, 4453-4 (1988).

<sup>20</sup> E. HEY-HAWKINS, U. DETTLAUF-WEGLIKOWSKA, D. THIERY and H. G. VON SCHNERING, *Polyhedron* **11**, 1789-94 (1992). See also T. VAN DEN ANKER, B. S. JOLLY, M. F. LAPPERT, C. L. RASTON, B. W. SKELTON and A. H. WHITE, *J. Chem. Soc., Chem. Commun.*, 1006-8 (1990).

<sup>21</sup> J. J. HARLAND, R. O. DAY, J. F. VOLLANO, A. C. SAU and R. R. HOLMES, *J. Am. Chem. Soc.* **103**, 5269-70 (1981).

<sup>22</sup> C. BRELLIERE, F. CARRÉ, R. J. P. CORRIU and G. ROYO, *Organometallics* **7**, 1006-8 (1988).

<sup>23</sup> K. M. MACKAY, B. K. NICHOLSON, W. T. ROBINSON and A. W. SIMS, *J. Chem. Soc., Chem. Commun.*, 1276-7 (1984).

<sup>24</sup> A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., Oxford University Press, Oxford, pp. 987-91 (1984).

<sup>25</sup> P. JUTZI, U. HOLTSMANN, D. KANNE, C. KRÜGER, R. BLOM, R. GLEITER and I. HYLAKRYPIN *Chem. Ber.* **122**, 1629-39 (1989).

<sup>26</sup> A. S. BEREZHAI, *Silicon and its Binary Systems*, Consultants Bureau, New York, 1960, 275 pp.

<sup>27</sup> B. ARONSSON, T. LUNDSTRÖM and S. RUNDQVIST, *Borides, Silicides, and Phosphides*, Methuen, London, 1965, 120 pp.