

Defects in silicon

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Abstract

The method of obtaining pure polycrystalline silicon is described, followed by short accounts of how this material is converted into single-crystal form either by the Czochralski (CZ) pulling method or the float-zone (FZ) method. It is shown that the silicon contains various impurities including oxygen, carbon, boron and possibly hydrogen. If a silicon nitride crucible is used instead of silica for the growth of CZ crystals they contain nitrogen. Crystals also contain structural defects derived from the aggregation of intrinsic point defects as they cool from the melting temperature. The defects and impurities often show a non-homogeneous distribution in the form of helical swirls. Heat treatment of silicon-containing oxygen leads to the clustering of this impurity. At 450 °C there is formation of small complexes that act as shallow donors. Investigations using IR and ESR spectroscopy have so far failed to determine the atomic configuration of the defects. Heating at higher temperatures causes wide-scale precipitation of oxygen. There are interactions with carbon and there can be formation of silicon carbide precipitates. Contamination from Cu, Au, Fe, etc, can occur during these treatments and methods for gettering these metals are discussed, involving dislocations and silica precipitates. Low-temperature irradiations produce vacancies and self-interstitials which combine with impurities to form complexes on heating from 4 K to 300 K. Certain defects, including vacancies and impurity interstitials, show athermal migration and unexpected electrical properties. Evidence is presented to illustrate the possible charge states of self-interstitials. Damage produced by fast neutrons is discussed next, followed by a brief account of neutron transmutation doping whereby naturally occurring ^{30}Si is converted to ^{31}P by the capture of thermal neutrons. Finally, some aspects of high-temperature diffusion are discussed and attempts are made to correlate the data with that derived from the irradiation studies. It is concluded that self-interstitials are important defects in silicon and oxidation of a surface generates a large flux of non-equilibrium defects which diffuse into the bulk crystal, leading to enhanced impurity diffusion and the growth of structural defects.

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1. Introduction

As the techniques for the purification of silicon were developed during the 1950s, followed by the routine growth of single crystals, a huge new research effort was born both in industry and in academic institutions. There were two prongs to the investigations: silicon proved to be a fascinating vehicle for the study of basic solid-state physics, enabling the testing and elaboration of a very wide range of theoretical ideas; just as exciting was the innovation and development of devices for power, circuits or other applications such as solar cells. These two areas of attack were by no means independent. The basic physics could only be carried out because of the availability of suitable material, containing the desired types and concentrations of impurities and crystalline defects. Likewise, the properties of devices, such as the current-voltage characteristics or the switching time of a diode or transistor, were found to be dependent on the detailed properties of the material used for their manufacture. It is clear that a balanced interchange of information was necessary for rapid progress to occur.

After about a decade there appears to have been something of a breakdown in this balance. Much of the physics and chemistry at the basic level had been explored, at least up to a certain degree of understanding. For example, once the band structure had been measured, it was possible to understand shallow donor or acceptor impurities; once the phonon dispersion curves were established, the vibrational properties of defects were investigated; in addition, studies were well advanced on diffusion, electron spin resonance and the electrical properties of defects giving rise to deep electronic levels and also of the effects of high-energy irradiation. However, the production of devices did not keep up because of technical problems associated with processing, involving surface damage, alloying of contacts, encapsulation, mask damage, pin-holes, etc. A view was often expressed, at least in some industrial environments, that the state of knowledge of the material was more than adequate to meet the requirements of the device engineers. It was at this time, around 1965, that the possibilities of other semiconductors such as gallium arsenide became evident and much fundamental work was then redirected towards these newer materials; it may be noted that the first International Symposium on GaAs was held in Reading in 1966 (Franks 1967). Nevertheless, progress was being made with the silicon devices as better manufacturing techniques were introduced and the demands on the devices by systems engineers became ever more stringent. Higher breakdown voltages were required for rectifiers, faster switching times were necessary and the dimensions of individual features in integrated circuits became smaller as we advanced towards medium-scale integration (MSI), large-scale integration (LSI) and now finally towards very-large-scale integration (VLSI). A stage was reached when much of the device processing could only be described in terms of recipes, often related exclusively to one manufacturer's routines.

There was further catching up to be done, but this time on the basic physics of the material and its processing; indeed the material had changed because of the introduction of large diameter crystals which were dislocation-free. Much of this later work which has sometimes involved second-order effects of originally 'well known results' has proved to be most stimulating and challenging; certain processes, once thought to be quite straightforward, have in fact proved to be exceedingly complex.

It is worth stating that there now exist a multitude of books on the use of silicon devices and their applications to systems: in addition, much has been written on the social and economic implications of the silicon 'chip'. But few books have appeared on the subject of silicon material and this is not because the omission has escaped the notice of publishers. The reason is that such a 'book' would now have to consist of several large volumes because of the amount of material to be covered. Fortunately the material of each such volume can be found diffused throughout conference proceedings and previous review articles. The writing of the present article entitled 'Defects in silicon' appears therefore to be not just over-ambitious but quite impossible. It is clear that constraints have had to be imposed and a particular theme chosen. The theme is inherent in the discussion already presented and it is to give a description of defects present in as-grown material and in material following certain processing required for the manufacture of devices in a broad sense. We shall follow silicon through heat treatments, high-energy irradiations and diffusions. The two latter topics are of course interrelated because of the common involvement of vacancies and self-interstitials. Certain aspects will be selected for more detailed discussion although such a selection must inevitably be highly subjective. Consequently it would seem from the outset that apologies are in order to those workers whose results will not be deemed to have been given adequate space or in some cases their work may not even be mentioned in spite of its importance.

The categories of defects to be considered have to include (a) isolated impurity atoms occupying substitutional or interstitial sites, (b) isolated lattice defects, namely vacancies or interstitials, (c) aggregates of two or more impurity atoms, (d) aggregates of two or more intrinsic defects, such as a divacancy, (e) complexes of impurity atoms with lattice defects, (f) larger aggregates or complexes, which in effect constitute a second phase or a precipitate, and finally (g) dislocations which may be in the form of small loops as an alternative to the long glissile variety forming a grown-in network.

We have to work with a material that is never completely pure, and which always contains a range of defects although a particular one may be predominant. We shall find that impurities can cluster or precipitate and this process leads to structural defects. The latter defects may then act as nucleation sites for further interactions with impurities. It follows that the individual types of defect listed above are in no sense independent of each other.

The topics to be covered have been given in the contents list, and the treatment will be from the point of view of solid-state physics. There will be no discussion of amorphous silicon or ion implantation studies, and the sections on neutron irradiation will be brief. The sections on impurity interactions and irradiation damage produced by high-energy electrons occupy most space and would seem to illustrate the problems of complexity to which we have alluded. The section on diffusion is also quite short and we attempt only to state and illustrate the current position.

2. The production of monocrystalline silicon

2.1. Pure polycrystalline silicon

Chemical analysis of the solid matter of the Earth's crust shows that oxygen is the most abundant element at 46% followed by Si (28%), Al (8%), Fe (6%) and all other elements at lower levels (Taylor 1964). There is no world shortage of silicon but it

is present in an oxidised and impure form. To obtain elemental silicon, quartzite (silicon dioxide) is reacted with carbon in an electric arc furnace at a temperature close to 1800 °C. About 90% of the resulting material, termed metallurgical-grade silicon, with a purity of about 99% is used in the manufacture of steel. The remaining 10% is reacted with hydrogen chloride to form a wide spectrum of compounds which are then subjected to fractional distillation. Most of this material is used in the manufacture of silicon rubber, silicone waxes, paint, etc. The most pure fraction of trichlorosilane (SiHCl_3) with a boiling point near 31 °C and with metallic contamination reduced to a minimum is subsequently decomposed by a reaction with hydrogen gas at temperatures in the region of 1200 °C to produce semiconductor-grade polycrystalline silicon. Conversion of silicon compounds to silane (SiH_4) can also be effected and reaction of this compound with hydrogen at much lower temperatures leads to the deposition of amorphous silicon. Studies of this material are now widespread but are considered to lie outside the scope of the present article; for further information the reader is referred to Brodsky (1979).

Because of the current wide-scale use of silicon, the processing described has to be on an economic basis and so now falls naturally into the domain of chemical engineering. It follows that the supply of silicon raw material is mainly in the hands of a few large suppliers, who are of course responsible for the chemical purity of the material.

A final test of the quality of the polycrystalline silicon can only be made once it has been converted into single-crystal form. Consequently, the chemical industry has also set up its own crystal growing facilities, again on a large scale for economic reasons. We therefore have a situation where most users of silicon are entirely dependent upon a small number of suppliers, a very different situation from the early days when individual device manufacturers had their own crystal growing facilities.

2.2. *Monocrystalline bulk silicon*

Polycrystalline silicon is converted into single-crystal ingots by either the crucible-pulling Czochralski (CZ) technique or the crucible-free, floating-zone (FZ) technique. About 70% of the world's production is crucible-pulled and is preferred in the manufacture of integrated circuits although FZ material is more pure. However, the latter material has important uses for making high-voltage power devices, particularly following so-called neutron transmutation doping (NTD) (see § 6.2.).

2.2.1. *The Czochralski technique.* Polycrystalline silicon in the form of nuggets, or a one-piece crucible charge, is placed in a high-purity silica crucible which in turn is placed into a graphite heat spreader (see figure 1). The charge is then heated to the melting point (1420 °C) by a carbon resistance heater. The furnace atmosphere is high-purity argon, at either 1 atm pressure or more usually now at a lower pressure of 20 Torr. A rotating seed crystal of the desired crystallographic orientation is dipped into the melt which is rotated in the opposite direction to the seed. When suitably wetted by the melt the seed is withdrawn and allowed to grow outwards to the desired diameter by adjusting the pull rate and melt temperature. Early crystals had diameters of, say, 1 or $1\frac{1}{2}$ in but crystals with diameters of 3 or 4 in are now common and some crystals are grown even larger. A lot of operator skill is required at the beginning of the growth process but automatic diameter control systems allow CZ crystals to be grown close to the diameter required for finished wafers. It is important to realise

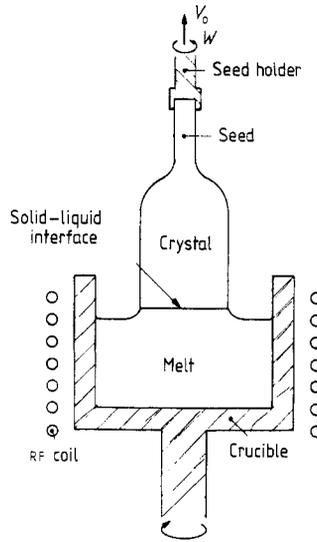
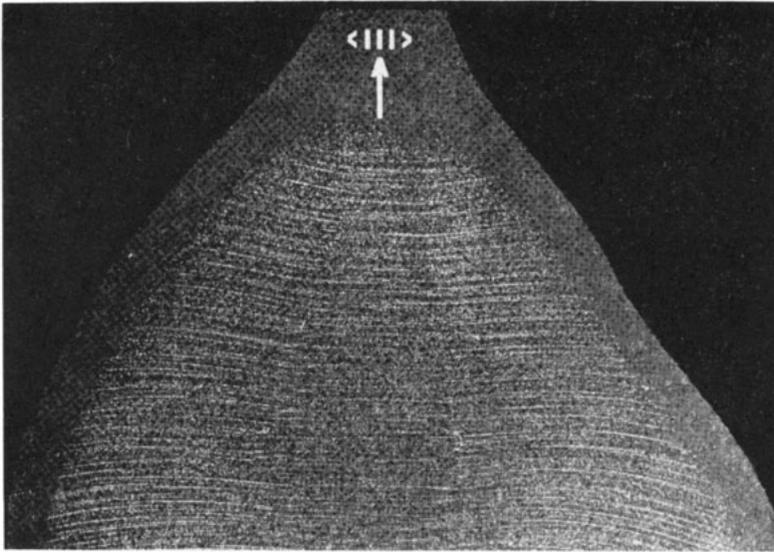


Figure 1. The Czochralski crystal growing method with a pulling rate V_0 and crystal rotation rate W . Heating is achieved by coupling from an RF coil as shown, or by passing current through a graphite element surrounding the crucible (see text). The seed crystal is necked to a small diameter in the early stages of growth so that glissile dislocations run out to the surface and are lost; the crystal then remains dislocation-free (after de Kock 1980).

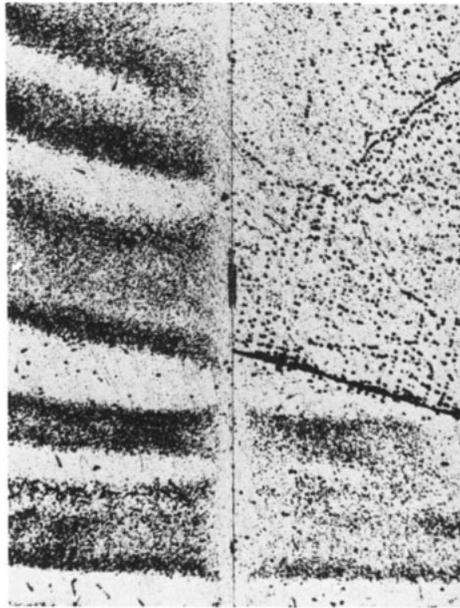
that, as the seed is rotated and withdrawn from the melt, a helical growth geometry is produced. Any small variation in the temperature around a circular path, concentric with the growth axis, would automatically produce periodic fluctuations in the growth rate. Such effects lead to the formation of defects located in helical swirls so that the final crystal is not homogeneous, as shown in figure 2.

The purity of CZ crystals is limited because of the thermal dissolution of the silica crucible which occurs throughout the growth process. Impurity atoms from the silica together with oxygen pass into the melt and some fraction becomes incorporated into the growing crystal. Because the silica crucible is supported by hot graphite, carbon monoxide may form at the interface and so allow carbon to be transferred to the melt and hence the crystal. It is clear that such silicon will contain several impurities, including oxygen near to its solubility limit, and there is the possibility of impurity clustering occurring as the hot crystal cools to room temperature. Although practically all CZ crystals known as zero-d (zero dislocation density) are now grown free from glissile dislocations using the Dash technique (Dash 1958, 1959) (see figure 1), complex interactions between impurities, vacancies and interstitials produce micro-defects which may include small dislocation loops and tangles; such defects are often also distributed in the swirl pattern. Doping of CZ crystals is usually carried out by adding electrically active donor or acceptor impurities to the molten charge. The presence of swirls then leads to resistivity striations.

2.2.2. The float-zone technique. In the FZ technique, heating from a radio-frequency induction coil establishes a molten zone of silicon which is moved vertically through a polycrystalline rod in either a vacuum or an inert gas which may contain a very small concentration of a dopant such as phosphine. Purification of the starting rod



(a)



(b)

Figure 2. (a) X-ray transmission topograph of a copper-decorated *longitudinal* section of a silicon crystal showing striations or swirls; note absence of defects near the external surface which acts as a sink for diffusing defects as the crystal cools (after de Kock 1973). (b) Chemically etched surface of a *transverse* section of a heated silicon bi-crystal showing typical swirl pattern; note absence of swirls near the grown-in semicoherent boundary and in the region of glissile dislocations on one side of the boundary revealed as larger etch pits (after Newman and Wakefield 1962, unpublished work).

takes place by the zone refining of impurities with segregation coefficients less than unity (Trumbore 1960), and by the outgassing of volatile impurities, such as chlorine and silicon monoxide. Any number of 'purification' passes may be used and high-purity material with a long minority carrier lifetime and a low oxygen concentration can be obtained because there is no contamination from a crucible. Crystal growth is initiated on a rotating seed and glissile dislocations can be eliminated by the Dash technique as for CZ crystals. Unfortunately, FZ silicon freezes from a melt of small volume, and hence low thermal capacity, and so it is much more difficult to obtain uniform microscopic growth rates and uniformity of doping than for CZ crystals. As a result, pronounced resistivity variations are usually observed on a microscopic scale in FZ crystals doped via the melt in the conventional way. Such striations (swirls) can result in much lower reverse breakdown voltages of diodes or thyristors than would be expected on the basis of the average resistivity of the material. The striations are therefore very important defects. The practical problem has, however, been overcome by the use of neutron transmutation doping (see § 6.2) as an alternative to chemical doping. Of course, swirls of microdefects evolved from lattice defects may still be present and it is found that the introduction of glissile dislocations during high-temperature processing occurs very readily in FZ crystals, which are mechanically softer than CZ material because of the absence of oxygen impurity. For further details the reader is referred to de Kock (1973, 1980).

2.3. Epitaxial silicon layers

Epitaxial silicon layers are usually deposited on wafers of monocrystalline silicon heated to high temperatures in a flow of silicon tetrachloride (SiCl_4) and hydrogen, together with suitable dopants such as phosphine or diborane (figure 3). Uniform

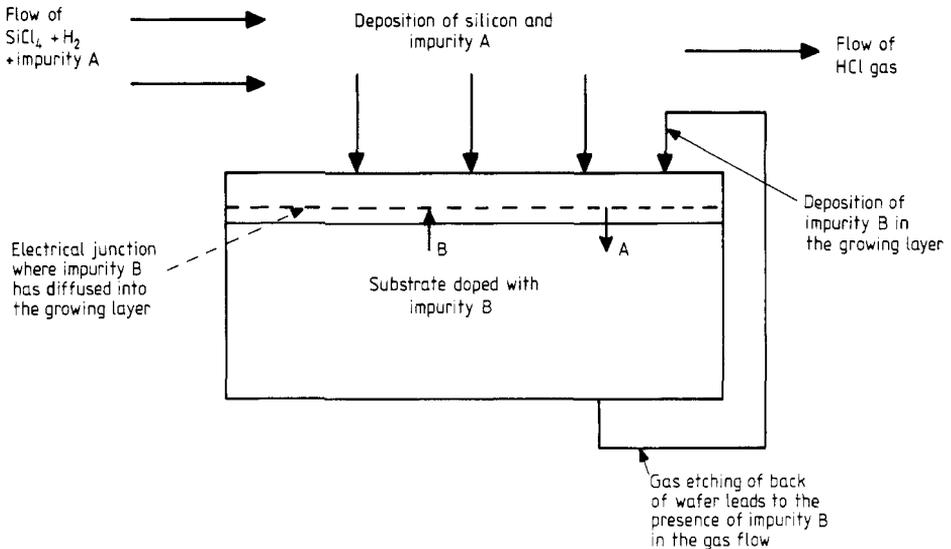


Figure 3. Deposition of epitaxial silicon at a high temperature of 1200°C by the decomposition of silicon tetrachloride and hydrogen carrying an impurity A in the form of a volatile component (e.g. BCl_3). The substrate silicon is doped with impurity B of the opposite conductivity type to A. The electrical junction may be in either the epitaxial layer or the substrate, depending on the diffusion coefficients and concentrations of A and B. Note also autodoping of impurity B (see text) and possible interdiffusion of oxygen and carbon.

heating of the substrate is required to obtain layers of a uniform thickness and also to minimise the risk of differential thermal contraction on cooling to room temperature. If this occurs the resulting stress can lead to the introduction of glissile dislocation networks. Other defects in the layer may be propagated from defects such as dirt on the surface or swirls in the substrate. Finally, interface defects may arise from misfit dislocations caused by small changes in the lattice spacing because of doping effects. In effect, epitaxial silicon is no different from bulk material but on the whole is likely to be less pure, and contain more crystal defects.

2.4. Summarising remarks

This short subsection on crystal growth has been presented so that the reader may understand what is meant by good-quality silicon. In general, references have not been given to individual topics; instead the reader who requires further information should consult the articles by Herrmann *et al* (1975), de Kock (1980) and the volume edited by Huff and Sirtl (1977).

At this point it would, however, be useful to elaborate slightly on the nature and the concentrations of the impurities present in the monocrystalline material as a prelude to more extensive discussion in later sections. We shall deal with the impurities first and then crystal defects.

In CZ material the main contaminant is interstitial oxygen, present in a concentration of about 10^{18} atom cm^{-3} (Kaiser *et al* 1956, Bosomworth *et al* 1970) which gives rise to the well-known $9\ \mu\text{m}$ infrared absorption band. This absorption has been calibrated so that a measurement of its strength can be used to determine the concentration of dissolved oxygen in any sample, provided it is not opaque due to the presence of a significant concentration of donor or acceptor impurities which lead to strong free carrier or photoionisation absorption. Carbon may also be present in either CZ or FZ crystals up to levels of 3×10^{17} cm^{-3} and can be detected to a lower concentration of 5×10^{15} cm^{-3} by measurements of the strength of a calibrated infrared absorption band at $16.5\ \mu\text{m}$ (Newman and Willis 1965, Nozaki 1974). Acceptors and donors present in nominally undoped crystals can be characterised by their infrared photoionisation spectrum measured with the sample at 4 K (Aggarwal and Ramdas 1965, Onton *et al* 1967) or from ESR measurements. The more recently developed technique of photothermal ionisation and the associated photoconductivity allows measurements to be made on thin epitaxial layers (see Skolnick *et al* 1974), and has the added advantage that minority impurities, such as phosphorus in partially compensated p-type material, can also be detected. These electrically active group III and V impurities also lead to characteristic photoluminescent lines (Nakayama *et al* 1980, Tajima *et al* 1981a, b) which are measurable for impurity concentrations down to about 5×10^{11} cm^{-3} . Various chemical procedures, such as activation analysis or electrical measurements based on the method of deep level transient spectroscopy (DLTS) (Lang and Kimmerling 1975), show that there is metallic contamination, usually at very low levels, although iron can be present in supplied wafers if they have received certain heat treatments subsequent to the growth of the crystal.

Swirl defects have been examined in considerable detail in pure floating-zone silicon. Slices of material generally exhibit two types of 'swirl' structure, broad bands being termed type A and narrow bands type B (de Kock 1973). Transmission electron microscopy (TEM) has shown that type A defects consist of interstitial dislocation loops without a stacking fault and having diameters up to $10\ \mu\text{m}$, local densities of

10^6 cm^{-3} and a Burgers vector $a/2 [110]$. The loops are occasionally decorated with impurity, but mostly not. TEM has not been successful in detecting the type B defects, suggesting that they are smaller than 50 \AA across. Petroff and de Kock (1975) have suggested that near the melting temperature self-interstitials are the dominant point defects, in agreement with the views of Seeger and Chik (1968), and as the silicon cools, the interstitials aggregate with carbon impurity to give clusters which constitute the type B defects. Subsequently these clusters collapse to give dislocation loops, initially with a stacking fault, but in the final stage the fault is eliminated. Three procedures have been successful in eliminating swirl defects from 'dislocation-free' FZ silicon ingots. First, the use of a hydrogen ambient during crystal growth suppressed the nucleation of the defects but the resulting silicon was found to be very brittle. Second, fast growth rates (5 mm min^{-1}) reduced the condensation rate because of an increased cooling rate. Third, slow growth rates (0.2 mm min^{-1}) allowed time for the point defects to diffuse to the crystal surface. It is interesting that all such swirl structures are eliminated if the ingots contain a grown-in dislocation density of only 10^3 cm^{-2} (see figure 2) and it is reasonable therefore to assume that the dislocations act as sinks for the diffusing defects (Bullough and Newman 1970).

The structure of swirl defects in CZ silicon is more complicated because of the presence of small precipitates due to oxygen (Petroff and de Kock 1975). When such particles are present during high-temperature processing local stresses can be set up and so cause a series of dislocation loops to be 'punched' out from the interface. The series of loops so formed generally move on $\{111\}$ slip planes along well-defined crystallographic directions and can extend up to distances of several micrometres from the nucleating particles (Tan and Tice 1976). This effect is similar to that reported by Jones and Mitchell (1958) for glass spheres in silver halides, for other effects in silicon (Dash 1958) and the theory has been given by Bullough and Newman (1960).

Thus we have encountered an interesting interplay between impurities and intrinsic defects. Dislocations can be generated by a precipitated second phase, while impurities are known to be attracted to dislocations by their elastic stress field so that they provide excellent nucleation sites for further precipitate particles. One can envisage a problem of space in the lattice: to accommodate a high density of interstitials (oxygen) locally, extra lattice sites must be created, while the aggregation of small substitutional atoms (carbon or boron) would be expected to lead to the generation of vacancies. There is also the surprising indication that self-interstitials are more important intrinsic defects than vacancies in silicon near to its melting temperature.

Irrespective of the fine detail, the conclusion is that silicon is not as chemically pure as might have been thought, is structurally inhomogeneous and may contain dislocation loops and other intrinsic defects.

3. Commonly occurring impurities

We stated in § 2 that silicon grown from silica crucibles by the CZ technique contains oxygen in a concentration of about 10^{18} cm^{-3} . 70% of all silicon is grown this way, and there have been extensive studies of oxygen in silicon which we shall discuss in § 3.1. Very recently crystals have been grown from crucibles of silicon nitride rather than silica and so there is a possibility of nitrogen contamination. Our knowledge of nitrogen impurities is very limited compared with oxygen, but we review the available data in § 3.2. A common impurity in all silicon is carbon which may be carried over

from the polycrystalline silicon used for crystal growth, or may be introduced via impure gaseous ambients. Its effect can be far reaching in device technology and there are still many uncertainties in relation to problems of solid-state physics (§ 3.3). We end this section with brief discussions of hydrogen and boron impurities. All silicon will have been exposed to hydrogen during its processing but little is known about this impurity in monocrystalline silicon. We shall show that, via ESR measurements, boron provides a useful indicator for the crystal perfection of silicon which can now be of an exceedingly high order; boron is a common contaminant from silica crucibles.

3.1. Oxygen

Isolated interstitial oxygen atoms are bonded to two silicon neighbours to give electrically neutral defects. The defects give rise to a sharp infrared absorption line at $9\ \mu\text{m}$ ($1136\ \text{cm}^{-1}$) with a half-width of less than one wavenumber at 4.2 K together with several other weaker bands. This spectrum is very complicated but has been explained in all essential respects and so the lattice dynamics will not be discussed here. For reviews the reader is referred to Newman (1973) and Pajot (1977).

When CZ silicon containing oxygen at a level of $10^{18}\ \text{cm}^{-3}$ is heated to 430–450 °C, there is formation of defects which act as donors with a low ionisation energy, the so-called thermal donors. It was found that the initial rate of production of these defects was proportional to the fourth power of the oxygen content, while the concentration of donors reached a maximum value, typically about $10^{16}\ \text{cm}^{-3}$, after heating for about 70 h, and was proportional to the third power of the oxygen content (Kaiser 1957, Kaiser *et al* 1958, Fuller 1959, Kanamori 1979, Cleland and Fukuoka 1981). A straightforward analysis based on rate equations led to the conclusion that oxygen impurities diffused to form stable clusters of four atoms which gave rise to the donor action. No reasons were advanced to explain why such a cluster should act as a donor, nor why somewhat larger clusters formed on heating to a higher temperature should be electrically neutral. From a practical point of view, the latter observation is very important. Crystals grown by the CZ pulling technique will spend some time at a temperature of 450 °C as they cool from their melting point to room temperature, and as a consequence there is formation of thermal donors. To eliminate such donors manufacturers sometimes reheat the material to, say, 650 °C and then cool it very rapidly through the 450 °C region (Capper and Wilkes 1978). It is clearly important to avoid metallic contamination in this process, particularly if cut wafers are heated rather than an uncut ingot, because in the former case there may be metallic diffusion to a significant depth into the surface regions which represent an appreciable fraction of the total volume.

It became apparent at an early stage that the donor centres did not have a unique structure. Thus, Hrostowski and Kaiser (1958) measured their infrared electronic absorption and found a multiplicity of lines, indicating the presence of several different species. This observation was confirmed by Bean and Newman (1972) and Helmreich and Sirtl (1977); the conclusion was and still is that various types of donors form sequentially during a period of heating. It is commonly found that the technique of electron spin resonance (Watkins 1975a) is invaluable in unravelling the atomic structure of defects, from observations of fine structure effects which allow the symmetry of a defect to be determined, and characteristic hyperfine splittings of levels which lead to the unambiguous identification of neighbouring nuclei. It is not surprising therefore that this technique has been applied to the thermal donor centres (Muller

et al 1979). Nine different paramagnetic centres, each with spin $S = \frac{1}{2}$, have been detected, but unfortunately with an absence of hyperfine splittings. For certain spectra, which have C_{2v} symmetry, two of the components of the g tensor exhibit a logarithmic dependence on the time for which the silicon was heated (figure 4). It is thought that

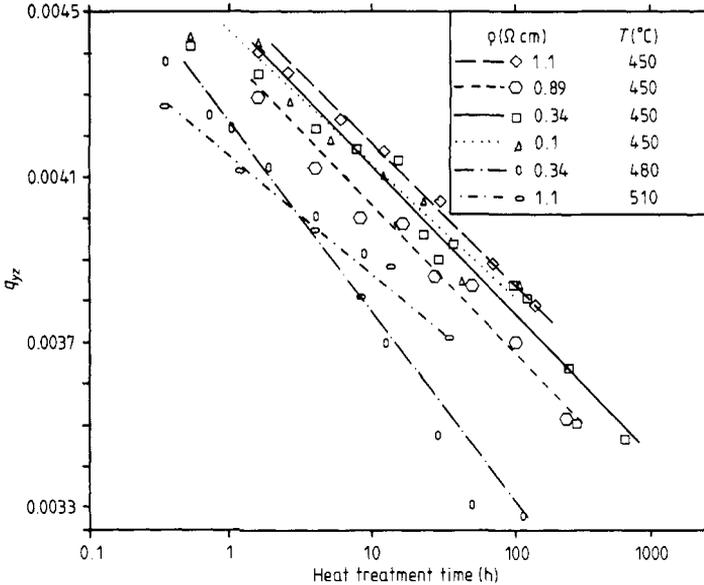


Figure 4. Component g_{yz} of an EPR donor spectrum as a function of heat treatment time for samples with different boron concentrations and for different heat treatment temperatures; for other details the reader is referred to the original paper (after Muller *et al* 1979).

there are several marginally different centres which exhibit ESR lines quite close together so that they overlap and that the distribution of centres evolves with time either geometrically or by the addition of extra oxygen impurity. Although these results have proved to be disappointing because they have not led to atomic models of the defects, they are consistent with the IR absorption data and the more recent photoluminescent data (Nakayama 1981). An important result was that the measured ESR g values did not agree with those found for oxygen-vacancy clusters observed in irradiated and annealed silicon. As a result, Muller *et al* (1979) were led to reject the proposal of Helmreich and Sirtl (1977) that the thermal donors were due to oxygen-vacancy complexes rather than just oxygen clusters. We are left with a fundamental problem in solid-state physics of explaining the donor property of the cluster. It is known for certain that the concentration of interstitial oxygen decreases during the heat treatment, so it is reasonable to conclude that oxygen is involved. It was suggested by Fuller and Logan (1957) that another fast diffusing impurity such as hydrogen might be complexed, but no evidence for this was found in the work of Bean and Newman (1972). The mystery still remains unanswered after 25 years of investigation.

On heating CZ silicon to higher temperatures of around 1000 °C, there is substantial removal of oxygen from solution. Heating samples to different temperatures for sufficient time to establish equilibrium should enable the solid solubility of oxygen to be determined from measurements of the IR $9 \mu\text{m}$ band made at low temperatures.

There are, however, discrepancies in the published data; for example, Hrostowski and Kaiser (1959) and Bean and Newman (1971) obtained heats of solution of 0.95 eV and 1.65 eV, respectively, although there was no difference in the absolute solubility at a temperature of 1250 °C. The measurements are inherently difficult to make due to background IR absorption, some of which arises from the growing oxide precipitates (figure 5). Because of the importance of the data it would be sensible to carry out these measurements again under modern clean conditions to avoid metallic contamination (see § 4). The precipitated second phase gives rise to Rayleigh scattering (Kaiser 1957) which is evident as a scatter loss in infrared transmission measurements in the spectral region 1–5 μm and there is a clear indication of preferential nucleation on dislocations (Lederhandler and Patel 1957) and stacking faults (Bullough and Newman 1963, 1970). Samples may be thinned and the precipitates may be detected by transmission electron microscopy, but in general, identification of the particles from a characteristic diffraction pattern is not possible as pointed out by Hu (1981).

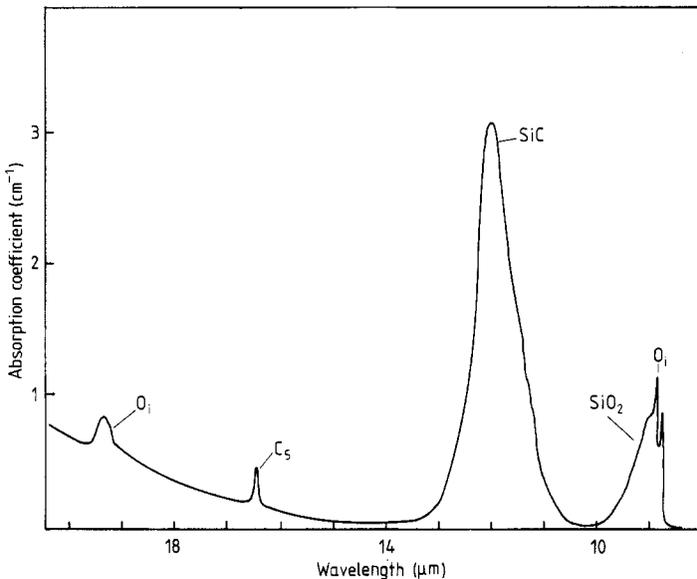


Figure 5. Infrared absorption in silicon after heating at 1080 °C for 100 h (two-phonon absorption features have been subtracted). Note strong absorption from precipitated SiC particles at 12 μm ; small residual absorption at 16.5 μm from substitutional carbon still in solution; absorption from interstitial oxygen in solution gives the band at 19.5 μm and a contribution to the total absorption at 9 μm ; other absorption at 9–9.5 μm is due to precipitated silica particles (after Bean and Newman 1971, unpublished work).

We have already stated that precipitated oxygen gives rise to relatively broad infrared absorption near 9 μm . This absorption has been investigated by Hu (1980) and interpreted in terms of the theory of Ruppini and Englman (1970) relating to small dielectric particles embedded in a medium of different refractive index. For particles of a size small compared with the wavelength of the reststrahlen, the formulation of lattice modes in terms of plane waves, characterised by the usual phonon wavevector q , is not appropriate. Instead an analysis in an alternative coordinate system, say spherical polar coordinates for spherical particles, should be used. For polar crystals there are then some changes in the usual vibrational frequencies

and various selection rules can be modified. Thus, the position of an expected band may be shifted somewhat and it can be broadened if there is a range of sizes or shapes of the absorbing particles. Hu (1980) has argued that the broad absorption near $9\ \mu\text{m}$ can be related to that of silica and that this provides an identification of the precipitates. A difficulty appears to be that silicon dioxide can exist in more than one crystalline form, or it may be amorphous. However, oxygen always forms bridges between pairs of silicon atoms and the characteristic vibrational frequency of this unit is always around $1100\ \text{cm}^{-1}$ ($9\ \mu\text{m}$), so that it would be very difficult to distinguish between various models.

There is at the moment an explosion in interest in the behaviour of oxygen in silicon as pointed out by Patel (1981) and there are gaps in our fundamental knowledge relating to the nucleation of precipitates. There has been much recent speculation in the literature that carbon impurity atoms act as preferential sites for nucleation, based partly on circumstantial evidence, but also on the fact that carbon can be lost from solution when oxygen precipitates. Indeed, infrared studies have demonstrated the interaction of the two impurities when only two or three atoms are involved (Bean and Newman 1972) but this technique does not give atomic detail for larger sized aggregates. It should be appreciated that a size or volume effect would be operative at the atomic level if carbon does nucleate oxide particles. Thus, carbon is a small atom in the lattice and from considerations of the elastic strain energy the local aggregation of interstitial oxygen would be favoured (Bullough and Newman 1970), a point discussed again recently, for example by Hu (1981). Much work is in progress and no doubt clarifications will emerge.

3.2. Nitrogen

The group V elements P, As, Sb and Bi all occupy substitutional sites in silicon with T_d symmetry and act as shallow donors (see Milnes 1973). The behaviour of nitrogen, on the other hand, has remained obscure over the years although it is known that nitrogen forms a stable chemical compound with silicon, i.e. Si_3N_4 . Attempts to dope silicon with nitrogen during growth, for example by the addition of a small concentration of a reactive gas such as ammonia to the ambient, results in formation of this compound. Any electrical effects appear to be so minimal that they would be difficult to distinguish from the effects of unwanted contamination. The early conclusion of Kaiser and Thurmond (1959) was that the solubility was negligible. Trumbore (1960) has shown that the solubility of impurities may be related to their covalent radius and extrapolation of the data for the known group V impurities to nitrogen would suggest a solubility of less than $10^{16}\ \text{cm}^{-3}$. However, if nitrogen were to act as a shallow donor there would be no problem in its identification at this or lower concentrations, by more than two orders of magnitude, as the ESR technique would provide adequate sensitivity.

More recently, efforts have been made to study nitrogen in ion-implanted silicon following annealing treatment up to $700\text{--}900\ ^\circ\text{C}$ to remove the radiation damage. An excellent summary of data has been presented in the introduction of the paper by Mitchell *et al* (1975). There is some consensus that the layers have 'n-type' properties, but that only about 1% of the implanted nitrogen led to electrical activity and that it would be necessary to differentiate between isolated nitrogen atoms and more complex defect aggregates. Mitchell *et al* went on to describe their own work and they recognised the need to use oxygen-free silicon to avoid problems of thermal

donor formation during subsequent annealing which may have masked the effect being sought. They found no electrical activity for implants of less than $10^{13} \text{ N}^+ \text{ cm}^{-2}$. At higher doses in the range 3×10^{13} to $5 \times 10^{14} \text{ cm}^{-2}$, about 1% of the nitrogen acted as a donor with an ionisation energy of 0.017 eV, which is difficult to understand because it is so much lower than the hydrogenic value of about 0.05 eV found for the conventional donors. At higher doses still, there was again a loss of electrical activity. At a dose of 10^{14} cm^{-2} the nitrogen would be located in a region about 2000 Å in thickness just below the surface in a concentration of about $5 \times 10^{18} \text{ cm}^{-3}$. The electrically active nitrogen would therefore have a concentration of the order of $5 \times 10^{16} \text{ cm}^{-3}$, rather larger, but similar to the solubility limit estimated above.

Recently it has been found that crystals grown by the floating-zone technique in an atmosphere of argon and nitrogen exhibit two very weak infrared absorption bands at 963 and 764 cm^{-1} (Abe *et al* 1981). The same bands are present in cz silicon grown from a silicon nitride crucible (Watanabe *et al* 1981b) and their strength has been correlated with the total nitrogen content of the samples although the configuration of the impurity has not been determined. If both bands are from the same defect centre, it must have an axial symmetry and it is of some interest that the frequencies are close to that of 943 cm^{-1} reported for the compound Si_3N_4 by Kaiser and Thurmond (1959). The solubility limit for this bulk material, determined by fast-particle activation analysis, was again about $10^{16} \text{ atom cm}^{-3}$ (Yatsurugi *et al* 1973). An important technological result of this work was that the presence of nitrogen inhibited slip in heat-treated samples, even though there was little electrical activity.

A vital breakthrough was made by Brower (1980). He studied FZ silicon where the surface had been implanted with 160 keV silicon (^{28}Si) ions to a dose of $4 \times 10^{15} \text{ cm}^{-2}$ to render it amorphous and the layer was then recrystallised using the technique of laser annealing. A ruby laser giving a Gaussian shaped pulse with a full width at half-power of 15 ns and 2 J cm^{-2} was used for this purpose. An ESR examination revealed the presence of a spectrum due to isolated ^{14}N atoms which are 100% abundant with a nuclear spin $I = 1$. The centres had C_{3v} symmetry and there was clear hyperfine and superhyperfine interactions with the 4.7% abundant ^{29}Si atoms of the substrate. The defect resembles in every way that of nitrogen in diamond discussed by Smith *et al* (1959). There was clear evidence that the extra electron was located along a $\langle 111 \rangle$ axis and thermal reorientation occurred at low temperature, showing that the nitrogen was not paired with another impurity or a native defect. The explanation is very simple. There is inadvertent contamination of the ion source by nitrogen and $^{14}\text{N}_2$ molecules are implanted together with ^{28}Si , as they have the same mass. The fraction of implanted nitrogen atoms was estimated to be 0.1% so that the total nitrogen implant would have been 4×10^{12} . This would lead to a peak concentration of around 10^{17} cm^{-3} . Presumably this is a supersaturated solution as the ESR spectrum disappeared on heating the sample to 430°C when a different spectrum was generated. Both resonances were absent after further anneals at a temperature greater than 600°C . Finally, optical excitation of the centres showed that reorientation occurred at 7 K for $h\nu > 0.5 \text{ eV}$, indicating that the nitrogen is a deep donor, again like nitrogen in diamond. This result makes it all the more difficult to interpret the low activation energy found by Mitchell *et al* (1975).

Other work involving laser annealing of implanted layers has been reported by Cullis *et al* (1980) who examined samples by transmission electron microscopy. They again found a relatively low percentage of electrical activity but no evidence for silicon nitride precipitation.

Further work to understand the behaviour of nitrogen is currently in progress. Many of the results discussed above have been confirmed, and new photoluminescence spectra associated with nitrogen have been found by Tajima *et al* (1981b). It is difficult at this stage to make predictions, but clearly there is a possibility that silica crucibles may be replaced by silicon nitride crucibles for the routine growth of CZ silicon for certain applications. If this should occur it would represent a break with tradition extending over nearly 30 years.

3.3. Carbon

Early determinations of the concentration of carbon in silicon using chemical or mass spectrographic methods yielded values in the range 10^{18} – 10^{19} atom cm^{-3} (Papazian and Wolsky 1956). It is now known that these values are above the solubility limit, but nevertheless single crystals of silicon were certainly produced with carbon contents of up to 2×10^{18} cm^{-3} , presumably as supersaturated solutions. The lattice location of the carbon in the as-grown material was not known at that time and so studies with ^{14}C were carried out to determine the activation energy for diffusion (Newman and Wakefield 1961). The measured value of 3.15 eV was slightly smaller but similar in magnitude to those found for the diffusion of the substitutional group III and V impurities (see Milnes 1973) and it was concluded that carbon atoms also occupy substitutional sites. This result agreed with the later findings of Baker *et al* (1968) that the presence of small carbon atoms in silicon leads to a reduction in the value of the lattice parameter by one atomic volume per carbon atom. It should be noted that when oxygen is present, there is an increase in the lattice parameter (Bond and Kaiser 1960) and so x-ray measurements alone do not allow the concentrations of carbon and oxygen to be determined independently.

Because carbon is a substitutional group IV element it is electrically neutral and there is no static dipole moment because of the tetrahedral symmetry. Consequently in the early days it was sometimes implied that there would be no infrared absorption due to the vibrations of the impurity. Comparisons were made with boron impurity atoms present in the negative charge state in exactly compensated crystals (Angress *et al* 1965). Infrared absorption due to these defects was attributed to a coupling of the electric vector of the incident radiation to the static charge (Dawber and Elliott 1963a, b). The true situation was made clear by Leigh and Szigeti (1967, 1968) who pointed out that it was not the static charge that mattered but quantities that they called apparent charges. Thus the overall apparent charge for a particular normal mode is the dipole moment per unit displacement in the corresponding normal coordinate; this can be related to individual atoms if the normal coordinates are known. Physically, when the carbon nucleus moves, it is relative to the bonding electrons and it is obvious that for certain modes a dipole moment is produced.

The lattice dynamical problem was analysed by Dawber and Elliott who predicted frequencies for the localised modes of vibration of the sequence ^{10}B , ^{11}B , ^{12}C , ^{13}C and ^{14}C . The theory was in excellent agreement with the frequencies of the measured infrared absorption bands (Newman 1973) and provided further evidence that carbon atoms occupy substitutional sites. The vibrations of ^{12}C at a frequency 607 cm^{-1} (77 K) (figure 5) leads to absorption superposed on the strongest two-phonon lattice band of pure silicon (Johnson 1959). This explains why it took until 1965 before the carbon band was identified by Newman and Willis (1965), whereas the absorption band due to oxygen at 1136 cm^{-1} , in a spectral region where the background absorption

from silicon is low, was observed some nine years earlier. In retrospect, it was clear that absorption due to carbon was present in the spectrum published by Lax and Burstein (1955) and these authors actually comment that the total absorption near to $16.5 \mu\text{m}$ was sample-dependent.

The strength of the local-mode infrared absorption band was originally calibrated by comparing it with the concentration of ^{14}C in pulled crystals doped with the radioactive isotope (Newman and Willis 1965, Newman and Smith 1969). The results were somewhat surprising because the apparent charge for the localised mode of vibrations was found to have the high value of 2.5 times the unit electron charge. The calibration was substantiated later by Baker *et al* (1968) and more recently by Nozaki *et al* (1970), followed by Endo *et al* (1972) who used fast-particle activation analysis to determine carbon concentrations. The latter work yielded a slightly different result by 25% from the original calibration and forms the basis for all current calibrations.

Heat treatments of crystals containing high concentrations of carbon to temperatures in the range $1000\text{--}1250^\circ\text{C}$ leads to the precipitation of an internal second phase that can be detected by infrared microscopy. Precipitate particles protruding from surfaces etched in a mixture of hydrofluoric and nitric acids and examined by glancing-angle electron diffraction were found to be cubic β -silicon carbide (Newman 1960). The particles also give rise to absorption in the region of $12 \mu\text{m}$ near the reststrahlen band of the compound, but with some modifications due to their small size and the fact that they are embedded in the silicon matrix (Bean and Newman 1971, Endo *et al* 1972) (figure 5). The analysis of the observations is similar to that already discussed in § 3.1 for small particles of precipitated silica. We should add that absorption at $12 \mu\text{m}$ was observed in some early work of Balkanski *et al* (1960) but as this referred to polycrystalline silicon, the second phase of SiC may have been present in grain boundaries.

It is now generally accepted that the solubility limit for substitutional carbon is about $3.5 \times 10^{17} \text{ atom cm}^{-3}$ near the melting temperature of silicon, and that the solubility decreases with decreasing temperature with a heat of solution of 55 kcal mol^{-1} . The segregation coefficient is 0.07 ± 0.01 (Nozaki *et al* 1970, Bean and Newman 1971, Endo *et al* 1972).

In terms of devices, it has been found that the presence of carbon in the silicon can lead to detrimental effects which are not completely understood. However, it has been suggested by Akiyama *et al* (1973) that the growth of silicon carbide precipitates is responsible for 'soft' electrical characteristics of reverse biased p-n junctions.

There is direct evidence from infrared spectroscopy for the existence of close carbon-oxygen pair complexes in as-grown silicon (Newman and Smith 1969) and more complicated complexes are produced in heat-treated material (Bean and Newman 1972). In addition, it was reported that the presence of carbon in a crystal inhibited the formation of thermal donors attributed to clusters of oxygen atoms (see § 3.1), a result which was confirmed by Helmreich and Sirtl (1977). These various observations appear to lead to a contradiction. On the one hand, there is evidence that carbon helps nucleate oxygen clusters, but when this occurs there is surprisingly a reduction in thermal donor formation.

Carbon also interacts with all the group III acceptors to form defects that were previously labelled In-X (for indium) (Scott 1978, Baron *et al* 1979). The complexes behave as shallow acceptors but with a lower ionisation energy than the isolated group III impurity. It has been shown that the defects have trigonal symmetry (Jones *et al*

1981) and it is inferred that the carbon atom occupies a nearest-neighbour site to the substitutional acceptor. The degree of pairing is found to be greater than that expected from a random distribution of the two impurities indicating a positive binding energy. However, the nature of the interaction is not known as it is not obviously Coulombic nor can it be due to size effects because the covalent radius of indium is greater than that of silicon, whereas that of boron is much smaller.

The presence of carbon has been found to affect the behaviour of gold diffused into silicon (Hill and van Isegham 1977) and there have been other reports of carbon interactions with copper, etc. Again we have no explanations for the interactions.

It may be concluded that carbon is a very important defect in silicon and its concentration must be controlled carefully if devices are to be made successfully. From the point of view of solid-state physics there are still many unsolved problems. Some further comments about the role of carbon in the growth of epitaxial layers will be given in § 4.1.

3.4. Hydrogen

It has been stated that if crystals are grown in a hydrogen atmosphere there is an influence on the nucleation of intrinsic defects during cooling from the melting temperature. We are unaware of any reports of infrared absorption due to hydrogen in such samples, and it therefore seems likely that most of the impurity is present in the molecular form when it would have no dipole moment. Comparisons may be made with hydrogen introduced into samples by proton bombardment when local mode absorption in the region of 2000 cm^{-1} , characteristic of the vibrations of Si-H bonds (Dixon 1965, p 12, Stein 1975, Kleinhenz *et al* 1979, Picreux *et al* 1979) is observed. Displacement of silicon atoms from normal lattice sites by the incident proton beam will produce lattice defects including clusters and it has been suggested that hydrogen atoms attach themselves to such defects or interstitial silicon atoms (Picreux *et al* 1979) to produce metastable configurations. Additional evidence that hydrogen plays an important role in saturating broken bonds is provided by the optical properties of amorphous silicon deposited from silane (SiH_4) as this material also shows infrared absorption in the region of 2000 cm^{-1} (Brodsky *et al* 1977). The mechanism of hydrogen interactions in as-grown silicon therefore remains unclear although many interactions have been found in germanium (Haller 1978).

3.5. Boron

Although boron has a small covalent radius and might be expected to have a low solubility, this is not so. The solubility is about 10^{21} cm^{-3} and the segregation coefficient is very close to unity (Trumbore 1960). Thus crystals uniformly doped with boron are readily prepared, making boron the preferred p-type dopant. The only problem that arises is that the lattice spacing of silicon decreases markedly when high boron concentrations are present and this can lead to the introduction of misfit dislocations, as for example during boron diffusion (Levine *et al* 1967, Watanabe *et al* 1981a). The presence of boron is easily detected from photoionisation spectra, bound exciton luminescence or by straightforward electrical measurements.

A point of interest is that boron, in common with the other group III shallow acceptors, cannot usually be detected directly by the ESR technique. The electronic ground state is a quartet $^4\Gamma_8$ derived from the top of the valence band which is

four-fold-degenerate ($J = \frac{3}{2}$). Because of inhomogeneous strains in crystals, arising from swirls and other impurities, the $^4\Gamma_8$ state decomposes into two Kramers doublets with a splitting different for each individual impurity atom. The Zeeman splitting is of a comparable magnitude and it follows that the resonance is effectively smeared out over a very wide range of magnetic field and cannot be detected. However, resonances can be observed in samples subjected to an external uniaxial stress to produce a splitting of the $^4\Gamma_8$ state large compared with that produced by the internal strains. The spectrum is then derived from the lower isolated Kramers doublet (Feher *et al* 1960). There is no reason why resonances should not be observed directly from a $^4\Gamma_8$ state if the internal strains are eliminated. Recently this has been achieved, indicating the great improvement in the quality of the as-grown silicon (Neubrand 1978a, b).

3.6. Résumé

The properties of light impurities expected to be present in silicon have now been reviewed.

The presence of boron acceptors is most easily observed because they act as shallow acceptors. The behaviour of nitrogen is quite different and it would appear that further studies are necessary; what is now certain is that this impurity is not a shallow donor and its solubility appears to be very low. The behaviour of residual hydrogen is not very clear, and comparisons with hydrogen in germanium are awaited.

Detailed discussions of carbon and oxygen have been given. Carbon substitutes for silicon to give a neutral defect with T_d symmetry. There is a large size mismatch and the solubility limit is about $3 \times 10^{17} \text{ cm}^{-3}$. Because oxygen is divalent it can bridge two silicon atoms, so saturating the bonding to give neutral defects with a solubility of about 10^{18} cm^{-3} . Oxygen atoms occupy interstitial sites and expand the lattice, whereas boron, carbon and nitrogen normally occupy substitutional sites and their presence reduces the lattice spacing. Interactions between elements are expected because of elastic strain fields in addition to Coulombic interactions. Oxygen and carbon impurities are unimportant in relation to the electrical properties of material, providing they are randomly distributed, but when they form complexes important changes can occur with the formation of thermal donors or acceptor X centres, etc. It has also become clear that the effects of high-energy irradiation can be quite dramatic, as discussed for hydrogen and nitrogen. Equally important is the fact that intrinsic defects produced by irradiation interact with almost all other known impurities, a topic which will be discussed in §§ 5 and 6.

4. Processing silicon

The fabrication of integrated circuits, diodes, thyristors, nuclear particle detectors, vidicons, charge-coupled devices, solar cells, etc, has one major feature in common. To produce the device, the silicon must be heated to a high temperature in the region of 1000°C . The processing involves only a limited number of techniques including epitaxial growth (see § 2.3), oxidation of the surface so that lithographic techniques can be used (Warner and Fordemwalt 1965, Mead and Conway 1980), diffusion of impurities across the surface, the introduction of impurities at the surface by ion

implantation followed by annealing (Mayer *et al* 1970), irradiation of samples by fast particles for other reasons followed by annealing, etc (Meese 1979).

4.1. *Effects of heat treatments*

The purpose of the annealing is three-fold. Firstly, to achieve epitaxial growth or oxidation, heating is necessary to obtain the required chemical reaction at the surface. Secondly, it is to increase the diffusion coefficient of some defect so that it has sufficient mobility to migrate the required distance during the time of the treatment. For example, if phosphorus is being diffused into boron-doped silicon it is necessary to tailor the profile to give a n-p junction at the required depth. Thirdly, following irradiation of samples by high-energy particles which leads to the displacement of atoms from lattice sites, it is usually necessary that the damage should subsequently be removed. It is not so much a matter of making primary defects more mobile, but of allowing metastable configurations involving perhaps clusters of vacancies to dissociate and annihilate with interstitials which may be clustered elsewhere in the crystal. The processes described seem at first sight to be quite simple. The complications arise because many processes will be operative at the same time, and the solubilities of most impurities in silicon have a maximum value just below the melting point and then decrease as the temperature decreases (Trumbore 1960, Milnes 1973). It is helpful to consider specific examples, some of which have been topical for many years.

Suppose we wish to deposit an epitaxial layer doped with impurity A onto the front face of a silicon wafer doped with impurity B (figure 3). At high temperature there will be inter-diffusion of both impurities (and host lattice atoms) at the interface so that a sharp junction will not be formed and its location could be either in the deposited layer or in the substrate. In addition, impurity B may diffuse out of the back of the wafer, be taken up in the gaseous ambient and then be redeposited in the growing layer (see the volume edited by Schroeder (1962)). The latter process, which is known as auto-doping, has presented serious problems in the design of equipment for epitaxial growth, particularly as the diameter of silicon wafers increased. If the substrate wafer is CZ material, oxygen will also diffuse across the interface, together with carbon if it is present. Indeed, surface contamination by the latter element detected by Auger electron spectroscopy, and perhaps present in the form of small silicon carbide particles, has been shown to lead to gross structural defects in epitaxial layers (Joyce *et al* 1969, Charig and Skinner 1969). When the substrate temperature was raised above a critical level so that the carbon in the silicon substrate was below the solubility level, the diffusion flow of carbon atoms was inwards and a 'clean' surface was produced; good epitaxial growth could then be obtained.

It might reasonably have been thought that the diffusion of phosphorus into silicon would be completely understood as it is one of the most common processes used for making junctions. For deep diffusions of several tens of micrometres (Fuller and Ditzenberger 1956), or for diffusions from thick phosphorus-doped epitaxial layers into the underlying bulk material (Ghoshtagore 1971) this is probably true in the sense that the diffusion profiles follow the usual mathematical solutions of the diffusion equation. But most studies have been related to shallow diffusions, where the simultaneous growth of an oxide at the surface and diffusion of oxygen into the samples leads to an almost unbelievable complexity. Profiles measured by radiotracer techniques and electrical methods are carried out after diffusion at different temperatures. There are often two components in the profile (figure 6) but the most disturbing

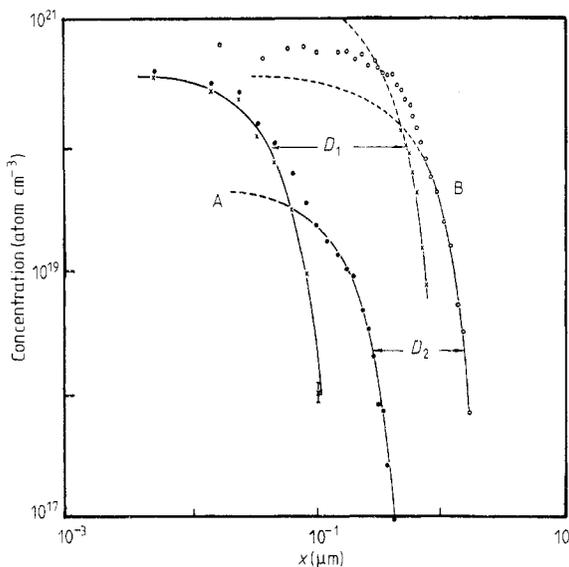


Figure 6. Diffusion profiles for phosphorus in silicon showing the typical double features due to non-equilibrium surface effects (after Peart and Newman 1973). A, $T = 900^\circ\text{C}$, time = 20 min. B, $T = 1080^\circ\text{C}$, time = 15 min.

feature is that the activation energy determined by different workers lies in the range 1.9–4.4 eV (for a review see Peart and Newman (1973)). It is clear that there are interactions with intrinsic defects generated near the surface and the details depend upon the experimental conditions. There is also frequently condensation of the defects to produce so-called oxidation stacking faults, often abbreviated to OSF. We shall return to this important problem in § 6.

The diffusion of oxygen in crystals has already been implied, and so there is the possibility of diffusion outwards from CZ crystals to form an external oxide layer on the surface. The concentration of dissolved oxygen just below the interface would then be equal to the solubility limit at the diffusion temperature. This process would denude a surface layer which might be used as the active region for a device. Precipitation of oxide particles in the interior of the crystal would also occur (as discussed in § 3.1) at the same time (figure 7). Direct observation of such particles in high-resolution transmission electron micrographs (Tan and Tice 1976, Maher *et al* 1976) shows that once formed they may generate small dislocation loops at adjacent sites which can act as sites for the growth of further oxygen precipitates. This topic has been repeated briefly because of its importance in relation to the 'gettering' of metallic contamination to be discussed below.

4.2. Metallic contamination and gettering

The anneals described are carried out in furnaces or epitaxial reactors for a specified time at the required temperature. Of paramount importance is the cleanliness of the wafer before it is heated and also that of the heating system. The most likely contaminants are metals such as iron, copper and gold (Theuerer *et al* 1957). All these metals (see Milnes 1973) and others from the transition group diffuse by an

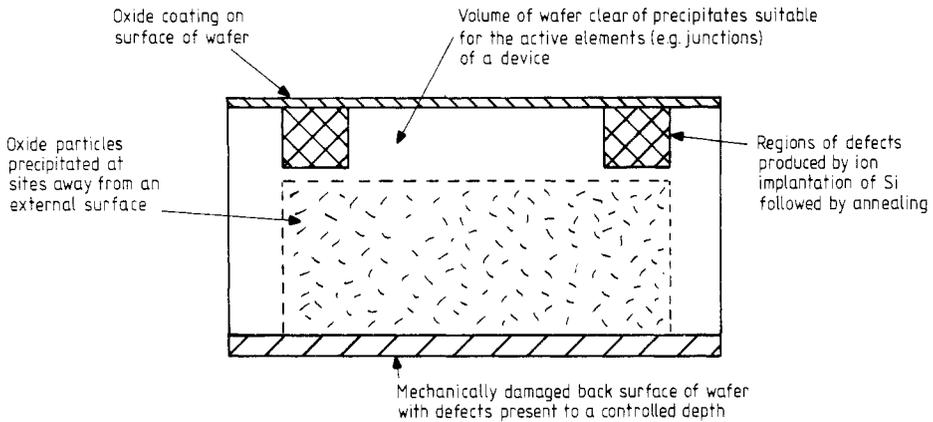


Figure 7. Diagram of a heat-treated and ion-implanted wafer of silicon showing the location of lattice defects and precipitate particles which act as nucleating sites for the subsequent precipitation of metals such as iron or copper. These regions get the regions in between which are the best locations for the active elements of planar devices.

interstitial mechanism which is sufficiently rapid that the impurity atoms are able to migrate completely through a wafer in a very short time at a temperature of, say, 1000 °C. There are, however, two types of behaviour. Each metal will have a certain solubility as an interstitial species and a different solubility as a substitutional impurity. Interstitial gold atoms were traditionally considered to combine with vacancies so that the impurity is transferred to substitutional sites at high temperature. Because vacancies are removed by this process, others are generated by dislocation climb or by the nucleation of dislocation loops (Dash 1960). (A current view might be that gold atoms interact rather with silicon self-interstitials—see § 7—but this would not affect the discussion here.) On cooling, the process is not reversible and much of the gold stays in the sample in a distributed form as an electrically active species that degrades the minority carrier lifetime. Copper and iron, however, show a different behaviour. They reach their solubility limit at high temperatures, but on cooling the samples, supersaturation is not maintained and rapid diffusion via interstitial sites again occurs. Aggregation of metal atoms takes place and there is precipitation of a second phase, probably an intermetallic compound with silicon. This may occur at an external surface if the sample is cooled very slowly or at internal points in the crystal for more rapid cooling. It has already been inferred that point defects may be attracted towards dislocations because of their long-range elastic stress field (Bullough and Newman 1970). Thus the cores of these structural defects act as excellent nucleation sites, and we obtain decorated dislocations that can be observed directly by infrared microscopy (Dash 1958, de Kock 1973). The growth of such precipitate particles is most undesirable technologically because if a precipitate straddles a p-n junction in a device it presents a short-circuit and the device does not work (figure 8). Consequently, techniques have been evolved to minimise the concentrations on unwanted metallic impurities that enter a crystal. In addition, those impurities that do enter are 'gettered': that is, they are made to collect or precipitate in selected regions away from the active regions of the device.

In the early days, silicon samples were heated in sealed silica tubes or in tubes with a continuous flow of an inert gas such as argon. It is now recognised that such

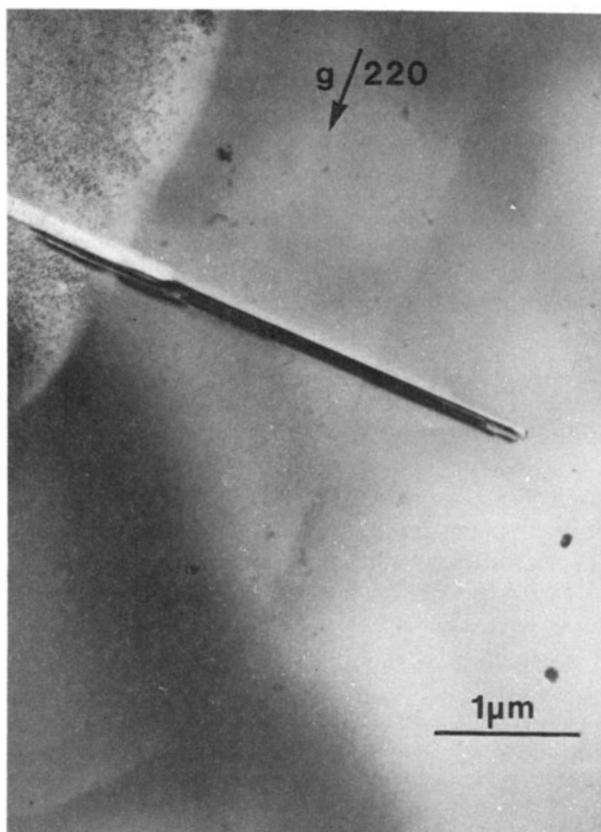


Figure 8. Precipitate particle containing a high concentration of Fe lying across a p-n junction as revealed by transmission electron microscopy (after Augustus *et al* 1980).

a simple arrangement is not satisfactory as the silica tube becomes porous to metals at high temperatures and this then leads to contamination of the samples. It is thought that such effects have led to problems in properly interpreting work on the electrical properties of a particular diffused metal in silicon because there may have been simultaneous diffusion of unwanted metals in comparable concentrations. As a result it would be very difficult to interpret, say, Hall effect measurements. To avoid such problems, samples are now first carefully cleaned and heated in double-walled furnace tubes. The ambient gas is passed over the samples in an inner tube and then led between this and an outer tube to sweep out contaminants which diffuse through the outer tube (Capper *et al* 1977).

The technique of 'gettering' is an 'art', involving a degree of commercial security, but the general processes are common knowledge. It is found that heat treatment of silicon in a clean sealed quartz ampoule may lead to an enormous degree of copper contamination, up to say 10^{16} atom cm^{-3} . If, however, the same treatment is performed under conditions where the surface of the sample is coated with an oxide layer containing phosphorus, the copper collects preferentially at or just below this surface and the bulk of the crystal remains relatively uncontaminated after it has recooled to room temperature. The process is much less efficient if the oxide contains other impurities such as boron rather than phosphorus. There has been speculation and

discussion about the mechanism of the process which is also effective for gold, iron and other metals (Meek *et al* 1975), but we shall not pursue these details. Alternatively, dislocations may be introduced into the wafer in carefully controlled regions so that designed precipitation occurs in these locations but not elsewhere. It is possible to start with dislocation-free silicon, and utilise mechanical damage of the back surface to introduce dislocations only into this region. Such damage may be produced by sand blasting, but its depth must be carefully controlled and there should be no movement of the dislocations throughout the wafer during later heat treatments; back-treated wafers have been available from manufacturers for some years. It is obviously sensible that the original silicon should be free of swirls as these too can act as nucleating centres (de Kock 1973). Dislocations are also formed in localised regions of the crystal which have been subjected to ion implantation followed by annealing (Mayer *et al* 1970). Thus localised implants can be made solely for the purpose of providing sites for precipitation in between active regions of a device. Finally, in CZ material we have already noted that internal precipitation of oxygen may lead to localised dislocation nucleation sites, but a zone near the surface of a wafer may be kept free of such defects. Thus the oxygen can be used to keep certain regions of a sample clear of unwanted metallic defects (figure 7) (Kishino *et al* 1980, Series *et al* 1981). In this respect CZ material has an advantage over the more pure FZ material, which explains why the former is preferred for the manufacture of integrated circuits where up to 10 or 12 successive high-temperature heat treatments may be necessary to fabricate a desired structure.

Although gettering is clearly of technological importance, it must be emphasised that the problem of unwanted, and often unknown, contamination is very real also in fundamental studies. These studies are sometimes carried out in laboratories where proper safeguards are not used to maintain the cleanliness of samples and there is therefore an uncertainty in the interpretation of the data. This topic illustrates very vividly how the device engineer made progress, mainly by empirical means, which were well in advance of the experimental techniques used by solid-state physicists. It is for this reason that a significant amount of space has been devoted to furnace treatments and 'gettering'. Fortunately new data relating to the properties of diffused metals from the transition groups, etc, are now becoming available (see Graff and Pieper 1981, Kimmerling *et al* 1981).

5. Intrinsic point defects and irradiation damage

5.1. Introductory remarks

A study of defects in any material should include the understanding of the properties of the intrinsic vacancy and interstitial. On the basis of thermodynamic arguments, such defects will be present in all crystals once they have solidified and a primary requirement is to determine their equilibrium concentrations as a function of temperature, so allowing the heats of formation to be evaluated. It is now known that the defects are extremely mobile in silicon and they are lost to sinks on cooling, so that quenching experiments are not very valuable in determining concentrations. We have, for example, already made reference to the nucleation of swirl defects and the climb of dislocations during gold diffusion treatments (§ 4.2). If impurities diffuse by a vacancy process it is also necessary to find whether there is a binding energy between

the two components. At first sight it would seem that it is only necessary to determine the activation energies for impurity and self-diffusion to obtain the answers. Such an approach is unfortunately naive because it makes inherent assumptions about the mechanisms of diffusion processes which may not be valid. In addition, it is certain that non-equilibrium processes are important, as evidenced by the anomalously high diffusion rate of phosphorus near a surface (§ 4.1).

An alternative approach is to introduce vacancies and interstitials by bombarding samples with electrons with just enough energy to cause lattice displacements. To obtain the maximum understanding, the irradiations should be carried out at the lowest temperature possible, of 4.2 K, to prevent thermal migration of the defects once they are produced, and low doses should be used so that damage events are well separated spatially. We should then generate vacant lattice sites with silicon interstitials located a short distance away. Such correlated Frenkel pair defects might be expected to annihilate rapidly by recombination if either component has the ability to migrate. However, the dissociation of some pairs will release the mobile species which may become trapped at sites adjacent to impurity atoms, or there could be aggregation of the defects to form larger and relatively stable clusters (figure 9).

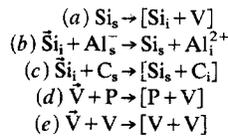


Figure 9. Series of reactions occurring in irradiated silicon followed by annealing treatments. (a) The generation of close interstitial–vacancy pairs (Frenkel defects) by electron irradiation; (b) the athermal migration of silicon interstitials which eject substitutional aluminium impurities into interstitial sites; (c) migrating silicon interstitials are selectively trapped by substitutional carbon impurities (see figure 10); (d) migrating vacancies are selectively trapped by phosphorus impurities to form a metastable pair; (e) two vacancies interact to form a di-vacancy.

It is crucial as a first step to determine the atomic configurations of the defects formed, using techniques such as ESR or IR spectroscopy. The second step is to relate the dependence of the charge state of the defect to the position of the Fermi level, thus enabling the ‘atomic’ observations to be linked to those obtained from electrical measurements. The latter data are most valuable when they are spectroscopic, in the sense that the concentrations of individual defect centres are determined, as in the technique of DLTS (Lang and Kimmerling 1975) rather than when they are macroscopic, as for example in Hall effect measurements. Once the concentrations of all the major defects are known, it is possible to study the dynamics of the system to give information about the diffusion rates, generation and annihilation of specific defects during annealing up to the highest temperatures. We might ask whether this ‘final’ state would correspond to the material in its as-grown state. One could anticipate differences because impurities in as-grown crystals normally form supersaturated solutions and aggregation to form new phases is expected if diffusion rates are enhanced by the presence of excess point defects such as vacancies.

There remains the problem of correlating these processes observed by spectroscopic techniques with other types of measurements of a more macroscopic nature, such as the use of radiotracers to determine the activation energy for diffusion, carried out

after treatments of samples at more elevated temperatures. This discussion is still in progress after many years but it is now certain that some intuitively held views are incorrect (see § 7).

5.2. Low-temperature electron irradiation

Irradiation of silicon at 4.2 K by 1–2 MeV electrons followed by an EPR examination with no intervening warm-up of the sample became established as an invaluable investigation technique about twenty years ago (Watkins 1965). Subsequently, there have been systematic studies of material that was originally p type or n type, doped with particular acceptors or donors, of material that contained oxygen or was relatively free of oxygen (float-zone crystals), of material doped with other impurities such as germanium, tin, etc. The literature is vast, making it impossible to discuss individual results here, but because the results are so comprehensive it is now possible to have an overview (Corbett *et al* 1977, Watkins *et al* 1979).

In n-type material an ESR spectrum is observed from the lattice vacancy, but not from the displaced interstitial atom so that no information is forthcoming about the latter defect. Similar experiments made on p-type material led to the identification of another spectrum arising from the isolated vacancy in the positive charge state, rather than the negative state found in n-type material. All was not straightforward however. In p-type material aluminium acceptor impurities were found to be ejected into interstitial sites at a rate equal to the generation of isolated vacancies. Direct collisions of incident electrons from the beam with these atoms could not be responsible because the probability of such events occurring was many orders of magnitude smaller than that observed. Watkins proposed that silicon interstitials, originally generated as partners in Frenkel pairs, somehow acquired mobility so that some pairs dissociated and the free interstitials were subsequently captured at sites adjacent to substitutional acceptor atoms. The two atoms then exchanged sites, with the silicon interstitial returning to a normal lattice site. This model is particularly appropriate to aluminium-doped silicon, as the resulting defect was unbonded interstitial Al^{2+} with T_d symmetry which showed a simple isotropic resonance and a fully resolved hyperfine splitting from the ^{27}Al ($I = \frac{5}{2}$, 100%) nucleus. The outstanding problem was to propose a mechanism to explain the mobility of the silicon interstitial at 4.2 K. The results for aluminium-doped silicon are the easiest to understand because in gallium-doped samples, no spectrum from isolated interstitial gallium impurities has been detected. It was therefore supposed that these defects were present but as Ga_i^+ , making them non-paramagnetic because all the electron spins are paired. This illustrates a short-coming of the EPR technique. It may be that mobile interstitials are trapped by other impurities such as carbon or oxygen, but such interactions would go undetected if the resulting defects are not paramagnetic. A further complication is apparent in boron-doped silicon. B_i^{2+} defects with T_d symmetry are not observed, but nevertheless, silicon interstitials are trapped by the boron acceptors. It has emerged that interstitial complexes are formed (Watkins 1975b) in which both atoms partake in the local covalent bonding; it suffices here to view the defect as consisting of two atoms which occupy one substitutional site with relaxations in the positions of the neighbouring shells of atoms. This is also the type of defect formed between carbon and a silicon interstitial atom found first from infrared measurements in a neutral charge state (Bean and Newman 1970) and later by EPR for a positive charge state in p-type material (Watkins and Brower 1976) (figure 10).

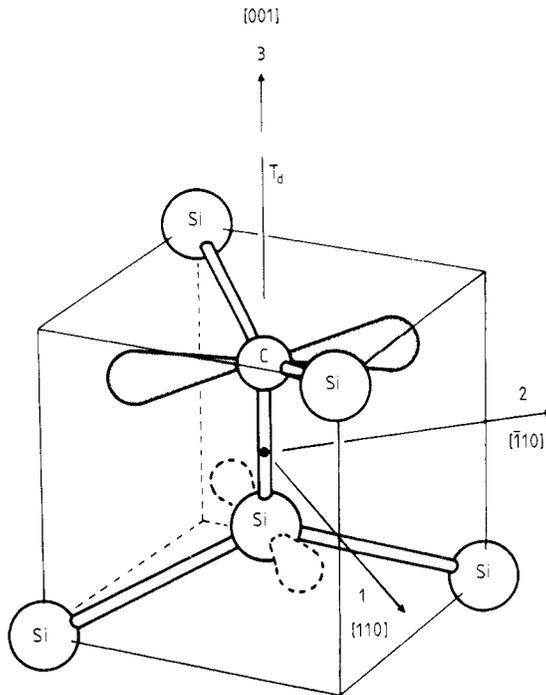


Figure 10. A model for the $\langle 100 \rangle$ carbon-interstitial silicon dumbbell showing the principal axes for the EPR spectrum (after Watkins and Brower 1976).

On warming samples after such irradiations vacancy migration occurs at surprisingly low temperatures. There is formation of divacancies and defects identified as nearest-neighbour impurity-vacancy pairs, with a concomitant disappearance of the spectrum from the isolated vacancies (figures 9 and 11). Vacancy motion occurs near 160 K in p-type material and at 70 K in n-type crystals, reflecting the effects of charge state on the migration process; the estimated activation energies are 0.33 eV (p type) and 0.18 eV (n type). It has been established that there is a positive binding energy of vacancies with most impurities including donors, acceptors and neutral oxygen, germanium and tin.

At even higher temperatures impurity-vacancy complexes, divacancies and interstitial complexes become mobile as entities and further interactions take place. For example, the defect Al_i^{2+} becomes mobile at about 200 °C and formation of $[\text{Al}_s^- - \text{Al}_i^{2+}]$ acceptor-donor close pairs occurs (figure 12). At a higher anneal temperature, these defects are eliminated although the mechanism is not known. It could be that a vacancy released from some other complex combines with the Al_i interstitial so that pairs of nearest-neighbour acceptors are generated, whereas in the as-grown crystal all the impurities were well separated spatially. We have no evidence for this particular reaction but there is no doubt that irradiation and annealing does lead to the production of close boron-phosphorus pairs in crystals doubly doped with these impurities (Bean *et al* 1972). Likewise, divacancies may coalesce to form much larger aggregates, some of which nucleate around oxygen atoms (see Corbett *et al* 1977). It is a view that has been held by some workers that electron irradiation of silicon leads to the production of simple defects and as a consequence the annealing is also simple and

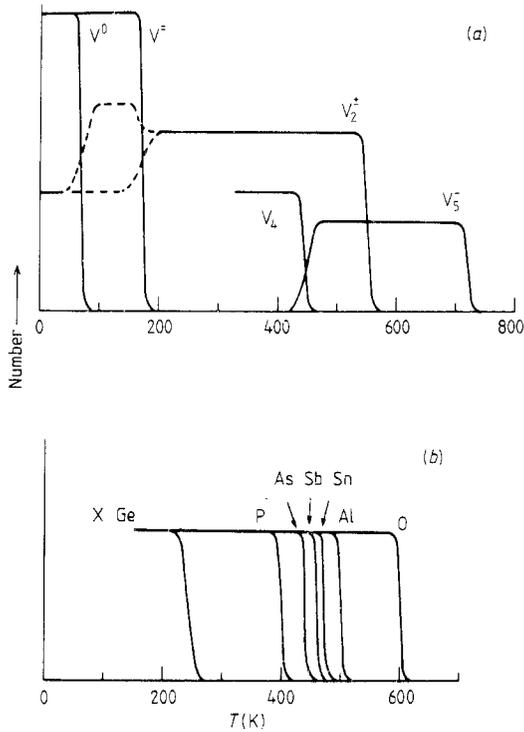


Figure 11. (a) The migration and aggregation of vacancies to form progressively larger clusters with increasing temperature of anneal following electron or neutron irradiation of silicon. (b) The selective trapping of vacancies by a range of impurity atoms and the anneal of the complexes at characteristic temperatures for dilute solutions (after Corbett and Bourgoin 1975).

is complete at a relatively low temperature. A large measure of recovery does occur at low temperatures but certain defect aggregates are likely to persist to temperatures up to, say, 800 °C.

The migration of phosphorus–vacancy pairs as entities is important in relation to the analysis of high-temperature diffusion data and so we should enquire how the conclusion was reached. The axis of such a pair defect is a silicon–silicon bond direction and for a random association there will be equal populations of defects lying along the four equivalent $\langle 111 \rangle$ axes. Because of the axial nature of the defect, there will be ESR absorption lines at different values of the applied magnetic field for defects with different $\langle 111 \rangle$ axes for an arbitrary direction of the field relative to the crystal axes. Thus the four geometrically equivalent centres can be distinguished. If now a uniaxial stress is applied along the $[111]$ direction, the energy of a defect having this geometrical axis will be different from defects lying along $[\bar{1}\bar{1}1]$, $[1\bar{1}\bar{1}]$ or $[11\bar{1}]$. On warming the crystal, the populations of defects will be modified to take account of this energy change. The sample is then recooled and the stress removed, leaving a metastable non-equilibrium set of defects. Heating the crystal so that the defects acquire some mobility allows re-orientation to occur to re-establish equal populations. The activation energies for such processes have been measured and are designated by E_R (Elkin and Watkins 1968, Van der Linde and Ammerlaan 1979). At higher temperatures still, there will be loss of the defects from the crystal and again an

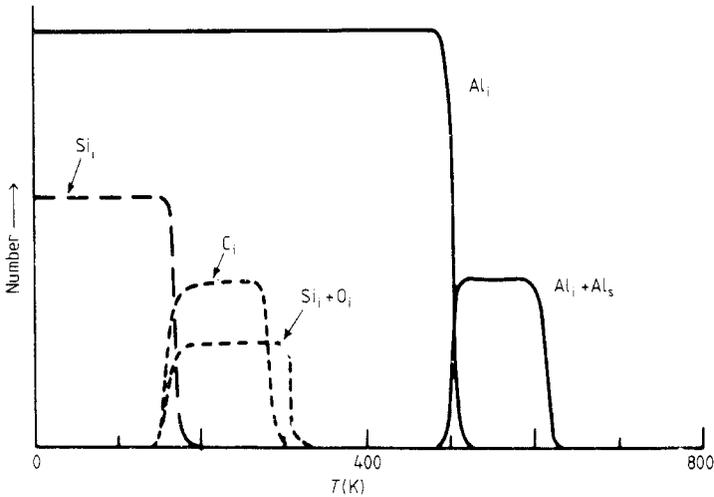


Figure 12. The selective trapping of interstitial atoms by impurities including carbon, oxygen and aluminium (see text) (after Corbett and Bourgoïn 1975).

activation energy may be measured, the so-called migration energy E_M . For [P-V], [As-V], [Sb-V], [Bi-V] and [V-V] it is found that E_R is equal to E_M , showing that the same process is operational in both types of motion (Hirata *et al* 1966, Yoshida 1971, Peart and Newman 1973). For re-orientation to occur it is necessary for the vacancy to move away from the substitutional impurity around a ring of lattice sites to the third neighbour position before it returns to another first neighbour site to regenerate the close pair defect (figure 13). It has been suggested, therefore, that long-range migration also occurs by this stepwise process. Such observations do not, of course, give information about very high-temperature processes as vacancies would not remain bonded to specific impurity atoms, and alternative diffusion mechanisms may be operative.

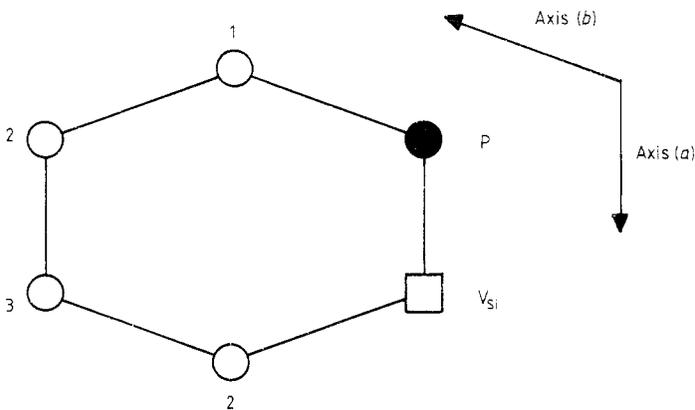


Figure 13. Puckered six-membered ring of silicon atoms viewed along a [110] direction showing a phosphorus-vacancy pair. V_{Si} must interchange with atoms Si(2) and then Si(3) in a clockwise sense before it can return to a crystallographically equivalent position at Si(1) but with a changed bond axis for the defect complex.

Before proceeding it would be helpful to summarise the information presented so far and to indicate the problems that have emerged.

It has been demonstrated that defects such as the vacancy, and also the divacancy, may be present in up to four different charge states. In p-type material the defects are positively charged because of the abundance of holes, while in intrinsic material, the defects become neutral, etc. At first sight these results correspond to expectations but a long-standing problem has been to explain how up to four charge states may occur for variations of the Fermi level over the very limited range of 1.1 eV, corresponding to the band gap of silicon. It was also necessary to explain why ESR spectra for certain charge states can be observed only under conditions of photoexcitation, suggesting that they may never be equilibrium states.

Answers to these important questions have been proposed recently by Watkins and Troxell (1980), following earlier theoretical work by Anderson (1975) and Baraff *et al* (1979). For certain defects in a particular charge state the lowest lying electronic level may be orbitally degenerate. The neighbouring atoms will then relax into a configuration of lower symmetry with a linear reduction in the electronic energy, because of the removal of the degeneracy. At the same time the elastic strain energy will increase, but only as the square of the displacements occurring in the relaxation. The result is that a new equilibrium is established with a net lowering of the energy which is known as the Jahn–Teller energy E_{JT} (figure 14). Watkins (1975c) has shown

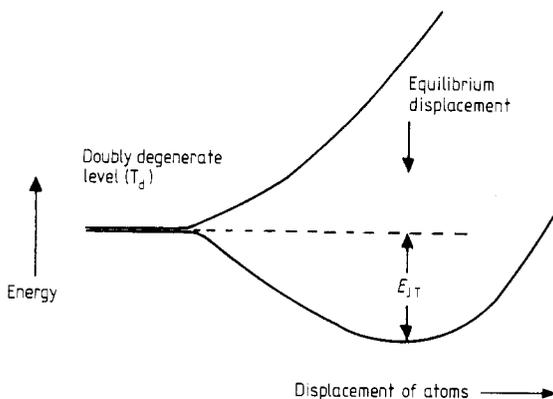


Figure 14. A doubly degenerate electronic level of the ground state of a defect showing a linear splitting as a result of a spontaneous distortion from tetrahedral symmetry for small displacements. Increases in energy quadratic with the displacements occur as the result of elastic forces. At equilibrium the reduction in energy is the Jahn–Teller energy E_{JT} .

that these energies may be larger than 1–2 eV for defects in silicon. Thus the addition of, say, a second hole to a positively charged vacancy will increase the energy because of the electrostatic repulsion, but this energy is offset by a reduction in energy E_{JT} . There is new evidence based on DLTS measurements that the energy of V^{2+} is actually lower than V^+ . If the overall charge compensation in the crystal implies that V^+ ought to be present, the compensation is obtained alternatively by having appropriate concentrations of V^{2+} and V^0 co-existing, because V^+ does not exist as an equilibrium state.

We next have to enquire about the location of interstitial atoms and the mechanism whereby they can migrate without acquiring thermal energy. A good starting point

is the early theoretical work of Weiser (1962) who investigated the diffusion of interstitial impurities. In the diamond structure there is an interstitial site with tetrahedral symmetry with four nearest neighbours and six next-nearest neighbours slightly further away. Situated midway between two such sites is another symmetrical 'hexagonal' site with six nearest neighbours (see the ring in figure 13) and eight next-nearest neighbours. Weiser made the assumption that the impurity would disturb the lattice bonding but would not disrupt it. If the impurity were electrically neutral the interaction with the lattice would be by short-ranged Born-Mayer repulsive potentials and the tetrahedral (T) site would be favoured because of its slightly larger size. However, if the impurity carried a static charge, dipoles would be induced on its neighbours leading to an additional attractive potential and the hexagonal (H) site would then have the lower energy. For diffusion to occur the sequence would have to be $H \rightarrow T \rightarrow H$ or $T \rightarrow H \rightarrow T$, depending on the equilibrium site. In Weiser's model the barrier to migration is related to the difference in energies of the impurity in the two configurations. It can be seen immediately that if the impurity could change its charge state sequentially it would migrate by an athermal process.

This is the idea put forward by Bourgoin and Corbett (1972) to explain the migration of silicon self-interstitials at 4.2 K and the process is now known as the Bourgoin mechanism. It is assumed that the defect can exist in more than one charge state and there is sequential trapping and detrapping of charge carriers generated by the ionisation which occurs throughout the period of electron irradiation.

The model discussed so far is oversimplified since elements such as boron, carbon and silicon itself would be expected to participate in the covalent bonding, contrary to Weiser's assumption. Various models have been suggested and the energy of each configuration has been calculated (Corbett *et al* 1973, Frank 1975, Corbett and Bourgoin 1975). The models include dumbbells where two atoms occupy one substitutional site (figure 15) and where the geometrical arrangement is found to depend on the charge state of the defect. Data for the self-interstitial are still not available but

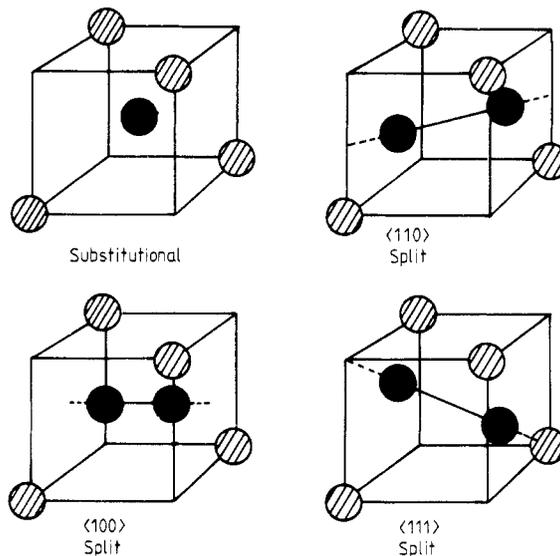


Figure 15. The principal split interstitial configurations in the diamond lattice. In a split configuration two atoms are equally displaced from a substitutional site (after Corbett *et al* 1973).

we have already cited work on carbon (figure 10) and there has been recent work on boron interstitials (Watkins and Troxell 1980, Troxell and Watkins 1980, Harris *et al* 1982). Studies of the annealing of this defect in the region of p-n junctions biased to give high levels of carrier injection so that non-equilibrium conditions prevail indicate that boron does indeed migrate by the Bourgoin mechanism. In addition, the defect is stable only as B_i^- or B_i^+ , presumably because B_i^0 is a high-energy defect irrespective of the various geometries that are available.

In summary, we have an explanation for the existence of multiple charge states of defects such as the vacancy in terms of Jahn-Teller energies, an explanation for a variety of lattice locations of interstitial atoms in terms of their charge state, and finally an explanation for athermal migration of interstitial species resulting from sequential changes in their charge state.

Some care is needed in the interpretation of radiation-enhanced (or induced) migration because another process may be operative. If a defect traps a carrier so that a non-equilibrium state is produced a second carrier will be captured at a later time to effect a recombination. The electronic energy released may then be taken up as motional energy of the atom to help overcome the potential barrier to reach a neighbouring site so that a 'diffusion' jump is effected. There is clear evidence for this process for defects in GaAs and GaP (Kimmerling and Lang 1975, Lang 1977), and we note that particularly for wide band-gap semiconductors the electronic energy may exceed the barrier height, leading to athermal migration.

It has been shown that vacancies may be either positively or negatively charged and it is not surprising therefore that they are attracted to either acceptors or donors to give $[A^-V^+]$ or $[D^+V^-]$ types of defects. Likewise, interactions via the elastic strain energy would account for the formation of $[O_i-V]$, $[Sn-V]$ and $[Ge-V]$ complexes; it is interesting that there is no evidence for the direct formation of $[C-V]$ pairs. The ESR and IR evidence shows that self-interstitials interact with acceptors, carbon and oxygen; from the latter interactions it could be deduced that the interstitial is either neutral or positively charged and there is some other evidence that this is so. A point of particular importance to the later discussion (§ 7) is that there appears to be no evidence for interactions of self-interstitials with donors such as phosphorus.

It has been implied and it is indeed true that radiation damage produces defects that have deep energy levels, some of which are hole traps while others are electron traps. This result leads to a simple explanation for the removal of carriers in material that is initially either n type or p type, although the actual carrier removal rate depends on the initial doping level and the conductivity type. Again the need to correlate energy levels with specific defects is apparent and can be achieved usually by the DLTS technique.

We might end this subsection by remarking that the presence of deep levels associated with damage defects can lead to photoconductivity at photon energies less than the band gap and also to reductions in the minority carrier lifetime. It would seem that the first of these effects may be useful in the fabrication of infrared detectors as pointed out by Gross *et al* (1973) and Maher *et al* (1982) for photoconductivity associated with divacancies. The second effect may also be useful for the control of the carrier lifetime in devices where conventionally metal diffusions have been used to obtain the desired effect. A discussion of this aspect has been given recently by Brotherton and Bradley (1981). Finally, we should also recognise that irradiation is in general detrimental to the performance of devices because of the induced changes

in their characteristics. For this reason much effort has been expended in trying to make certain devices as radiation-resistant as possible when, for example, they are required to operate for periods of many years in satellite systems which are subjected to continuous cosmic radiation.

5.3. High doses of electron irradiation at room temperature

The work discussed so far refers primarily to lightly doped crystals given electron doses up to 10^{17} electrons cm^{-2} . However, doping levels as high as 10^{20} cm^{-3} and radiation doses up to 10^{20} electrons cm^{-2} have been investigated. Under these conditions, the damage will be more complicated because successive displacement events will generate partially overlapping defects. In addition, it is not a practical proposition to carry out the irradiations with the samples at 4.2 K because of the small latent heat of liquid helium: indeed, very long irradiation times of the order of a day are required for a dose of 10^{18} electrons cm^{-2} with the sample mounted on a cold finger at 77 K. For these reasons most irradiations have been carried out with the samples kept at room temperature.

It could be asked whether there is any useful purpose in such investigations because they have apparently broken away from the fundamental 'simple' ideas outlined in § 5.1. In fact, the results to be discussed complement the fundamental results in certain ways and also form a link to data obtained for ion-implanted silicon and for crystals irradiated in a reactor with fast neutrons. Such material has now become commercially important, because of the use of neutron transmutation doping (NTD) to be discussed in § 6.2.

We start with the work of Angress *et al* (1965, 1968) who investigated the infrared absorption produced in silicon by the simultaneous presence of boron and phosphorus, or boron and other group V donors, in concentrations up to 5×10^{19} cm^{-3} . It is not possible to achieve exact electrical compensation between acceptors and donors because of the growth striations discussed in § 2.2. To eliminate the background free-carrier electronic absorption, the samples were therefore irradiated with 2 MeV electrons to doses of up to 5×10^{18} electrons cm^{-2} to introduce deep traps into the band gap. The resulting one-phonon absorption could then be observed as a continuum with specific features up to the maximum lattice frequency or Raman frequency ω_R , and sharp lines due to localised modes of vibration of boron (^{10}B and ^{11}B) above ω_R . It is implicit that all defects contribute to the absorption, including all impurities present and all the radiation damage defects, some of which will involve the impurities. Each defect species will give a different spectral distribution and the strength of the coupling to the incident radiation will also differ. It follows that there will be difficulties in making detailed interpretations of the data. Nevertheless, the pioneering work of Angress *et al* enabled certain features to be identified beyond any doubt: isolated boron atoms with T_d symmetry have localised mode frequencies for ^{11}B and ^{10}B of 621 and 644 cm^{-1} ; phosphorus gives a characteristic resonant mode at 441 cm^{-1} ; arsenic gives a similar mode at 366 cm^{-1} ; other continuum features have to be allocated to boron rather than the donor impurity present (Leigh and Sangster 1982).

Of most importance in the present context was the observation that a second dose of electron irradiation given to a sample after it had already been rendered transparent, led to reductions in the concentrations of boron and phosphorus atoms occupying normal substitutional sites with no nearby defects. This aspect was not pursued by Angress *et al* but formed the basis for later investigations of crystals containing

impurities other than boron, as well as more extensive studies of a range of boron-doped samples.

Bean *et al* (1972) have presented data showing the initial rate of removal of boron from normal sites as a function of the grown-in boron concentration. The removal rate (cm^{-1}) is defined as the concentration removed (cm^{-3}) divided by the electron dose (cm^{-2}), for samples of the order of 1 mm in thickness, which is somewhat less than the range of 2 MeV electrons in silicon. As the boron concentration increased from 10^{17} cm^{-3} to 10^{20} cm^{-3} , the removal rate increased from about 0.1 cm^{-1} to 3 cm^{-1} . The latter level corresponds closely to the rate of production of intrinsic defects in the irradiation, and implies that nearly all these defects form complexes with impurities at this high doping level. Bean *et al* postulated that vacancies were trapped by phosphorus and self-interstitials by boron. But we now know from the work of Watkins (1975b) that the boron interstitial is a mobile species at room temperature and it is strange that there was no immediate formation of boron-phosphorus nearest-neighbour pairs. These pair defects have been well characterised by their local mode absorption (Newman and Smith 1967, 1968, Tsvetov *et al* 1967, 1968, Pfeuty 1968, Newman 1973) and are generated when samples are annealed at a higher temperature of 200°C , corresponding to the anneal of [P-V] centres (see § 5.2) (also Kimmerling and Carnes 1971).

There is therefore an outstanding problem. What is the configuration of the 'lost' boron? Boron is a light atom and is expected to give rise to a localised mode of vibration in almost any arrangement. A possible conclusion is that boron interstitials form clusters during the irradiation and the absorption is spread over a wide spectral range and is perhaps weak because the associated dipole moment is small. More detailed measurements are described and a critical analysis of this problem has been set out by Newman and Totterdell (1974) and Laithwaite *et al* (1975); for a comparison with carbon, see figure 16.

Irradiation of FZ silicon doped with aluminium at a level of 10^{19} cm^{-3} (the solubility limit) has been investigated by Devine and Newman (1970). Because displaced aluminium atoms have been found to act as double donors, rapid carrier removal and eventual compensation was expected and indeed found. An ESR examination of the irradiated aluminium-doped samples showed that all Al_i^{2+} defects had formed close pairs with Al_s^- impurities during the course of the irradiation at room temperature. The fact that pairing occurred at a temperature lower than 200°C (§ 5.2) was attributed to a reduction in the diffusion distances when the impurity concentration is very high. This result is important because it illustrates the danger of characterising a particular annealing process by a particular temperature, as shown in figure 12.

A comparison of the data for the group III impurities with that for carbon is of interest because it has been established that substitutional carbon is displaced into bonded interstitial sites during irradiation and the C_i atoms become mobile near 270 K. There is then formation of a defect that gives rise to an electronic transition at 969 meV (Newman and Bean 1971, Konoplev *et al* 1977, Davies and Celeste do Carmo 1981). In addition carbon-oxygen complexes are produced if oxygen is present in the samples. It is found that the initial removal rate of carbon from solution is about an order of magnitude less than those for boron and aluminium from which it has been inferred that the silicon self-interstitial may carry a net positive charge; this topic has also been the subject of discussion by Watkins (1975c). Removal of carbon from solution leads to a similar problem to that encountered for boron. Quite simply, one may ask where does the carbon go? We know about the infrared absorption

from substitutional carbon, interstitial carbon, silicon carbide precipitates and carbon-oxygen pairs but the absorption in these features is either absent or insufficient to account for the concentration of carbon atoms lost (Brozel *et al* 1974). We are forced to the conclusion that some essentially non-absorbing cluster must be produced (figure 16).

In summary, we find that the presence of a high impurity concentration in silicon inhibits the recombination of Frenkel pairs produced by electron irradiation. Thus for a given dose, the residual damage is significantly greater, and in the limit can be as high as the number of atoms displaced in the primary collisions. It appears that the same basic processes occur as in lightly doped crystals in which interstitials interact with group III acceptors and carbon, while phosphorus probably forms pairs with vacancies. When both donors and acceptors are present they would appear to act as a sieve in separating the two primary intrinsic defects. Such observations complement those of § 5.2 but we have been left with the problem of the 'lost' boron and the 'lost' carbon for high doses. It has been suggested that clusters of impurities form and there is the possibility that such defects act as sinks for self-interstitials (see also Newman 1981).

6. Neutron irradiations

6.1. The nature of the damage

There have been many investigations of silicon after irradiation in nuclear reactors (see, for example, Meese 1979). This is in no sense a unique treatment and it should

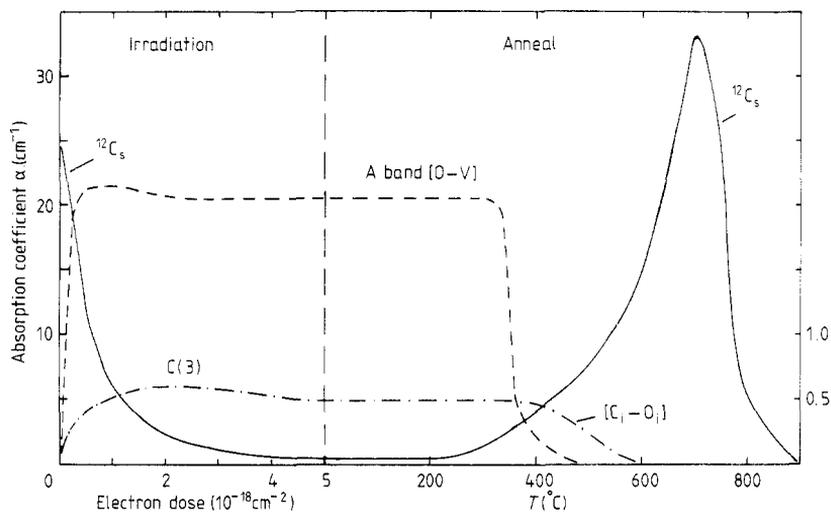


Figure 16. The effect of electron irradiation and annealing on a silicon sample doped with oxygen and a high concentration of carbon as revealed by infrared absorption spectroscopy. Irradiation reduces the concentration of substitutional carbon to a negligible value; there is production of small concentrations of [O-V] complexes and [$\text{C}_i\text{-O}_i$] complexes (right-hand scale of absorption coefficient). On heating, carbon returns to substitutional sites at about 700 $^{\circ}\text{C}$ but at higher temperatures there is precipitation of SiC. No absorption bands of adequate strength are found to account for the 'lost' carbon after high doses (after Newman 1981).

not be expected that the resulting damage should be well defined: the damage will depend on the particular reactor used and the position of the silicon in relation to the core or fuel rods in that reactor. A discussion of such differences has been given by Jung and Newell (1963). There will be a high flux of γ rays producing heat that can cause annealing of damage during the irradiation. The temperature of the silicon may be kept close to that of the cooling water provided there is good thermal contact, but otherwise the temperature may easily rise in excess of 100°C . The γ rays will also produce damage events rather similar to those produced by the electron irradiations already discussed. Other damage will occur as a result of host lattice atoms or impurities capturing neutrons and then undergoing a transition from an excited state to a lower energy state with the emission of a high-energy γ ray, β ray or even an α particle where the recoil energy causes a lattice displacement. Most damage will be caused by the direct collision of a fast neutron with a lattice atom, resulting in up to 10^3 displacements per event with the silicon interstitials moving outwards leaving behind a vacancy-rich and somewhat disordered zone (figure 17). The vacancies

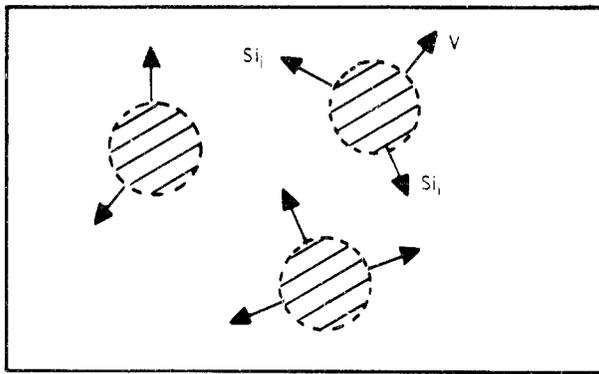


Figure 17. Vacancy-rich disordered regions produced at the sites of collisions of fast neutrons with silicon atoms. Silicon interstitials and some vacancies move into the surrounding matrix and are selectively trapped by impurities or other defects as in electron-irradiated material.

coalesce to form divacancies and larger clusters (Lee *et al* 1972, 1974, Lee and Corbett 1973), and there is some recombination with interstitials so that the resulting number of defects per collision is smaller than the number of displacements. For small neutron doses of up to 10^{17} cm^{-2} , adjacent disordered vacancy-rich zones will not overlap to any great extent and so we have to consider the damage as an inhomogeneous distribution. There are the highly damaged zones themselves and an outer matrix region where mobile interstitials and vacancies are captured by impurities as in electron-irradiated silicon. From this brief discussion it is clear that a full understanding of electron irradiation damage is a necessary prerequisite to the understanding of the damage produced by low doses of fast neutrons.

Nevertheless, the usual diagnostic techniques do sometimes show effects relating to the processes that must have occurred in the region of a primary collision. Thus, an ESR spectrum found for n^0 -irradiated samples, but not observed in electron-irradiated material, has been attributed to di-interstitials (Lee and Corbett 1974). IR spectroscopy shows absorption bands at 530 and 550 cm^{-1} which are probably vibrational in origin, and so would correspond to the localised vibrations of an intrinsic defect (Lappo and Tkachev 1971). In that case, the defect would have to be of an

interstitial nature because the bonding would be weakened around a vacancy leading to reduced local force constants and vibrational frequencies below the maximum lattice frequency (Raman frequency) of 520 cm^{-1} . Other observations are less direct, as illustrated by measurements relating to the divacancy.

In electron-irradiated silicon ESR and IR measurements of electronic transitions of V_2 defects show that all the defects can exhibit the geometrical reorientation described in § 5.2 and, in addition, the charge state depends on the concentration of shallow donors or acceptors present in the as-grown crystals (Watkins and Corbett 1965, Cheng *et al* 1966). In n^0 -irradiated material this is still true for the divacancies present in the matrix, but not for those in the disordered regions. The latter defects lose the ability to reorient under an external stress because of much higher internal stresses produced by neighbouring defects and the defect concentration is so high locally that the Fermi level is controlled by the defects and not the impurities (Daly and Noffke 1971). Thus the core and matrix regions can be distinguished, although not easily, and certainly not by means of a single 'quick' measurement.

On increasing the dose of fast neutrons above 10^{18} cm^{-2} up to 10^{20} cm^{-2} (Vook and Stein 1969) the vacancy-rich regions overlap and the damage becomes more homogeneous. At the highest doses, a simple calculation shows that almost every lattice atom will have been displaced at least once, although the silicon remains crystalline. The rate at which the displacements occur is sufficiently slow to allow substantial self-healing of the damage, thus preventing the transformation to the amorphous state as is found after the implantation of heavy ions. Spectroscopic studies of irradiated undoped material have shown that divacancies and larger vacancy clusters are still predominant defects. Estimates of defect concentrations made from such observations have been found to agree well with numbers estimated from small-angle neutron scattering (SANS) (see, for example, Beddoe *et al* 1979) used as an absolute diagnostic tool.

The presence of strain in irradiated samples can be detected by x-rays, infrared spectroscopy and electron microscopy but in the past, the range of techniques brought to bear on individual samples has not been adequate. For example, differences in the results of electron microscopic studies have been reported concerning the presence of small clusters and dislocation loops which may relate to the temperature of the silicon during irradiation. Without parallel infrared data it is impossible to test whether *in situ* divacancy annealing could account for the differences as suggested by Newman (1981).

Some n^0 irradiations have also been carried out on samples containing high concentrations of boron, phosphorus or carbon with a view to determining the fate of the impurities. Such data, obtained from bulk material, give a link to effects occurring in ion implantation but where the region of interest is constrained to a layer at the surface less than $1\text{ }\mu\text{m}$ in thickness so that it becomes very difficult to make use of standard spectroscopic techniques (Vook and Stein 1969). One may summarise the results by stating that local mode absorption for both boron and carbon is lost, as in electron-irradiated material, and phosphorus also becomes involved in complexes. Annealing of either the n- or p-type material to a temperature close to $1000\text{ }^\circ\text{C}$ is required to restore the original conductivity. Again we have the problem of not knowing the configuration of the impurity atoms in the damaged host and this must also be so in ion-implanted layers. In the latter case measurements made by the Rutherford back-scattering technique to determine the lattice location of impurities may yield different results from those obtained from ESR. As an example Watkins

(1975b) has discussed data for boron in ion-implanted silicon, boron in heavily electron-irradiated silicon and in lightly electron-irradiated material. The conclusion was that the data were not easily reconcilable and there is a need for further information. Finally one might add that the use of the back-scattering technique must be approached with caution, as the probing beam of ions can itself cause damage which may alter the sample significantly (Rimini *et al* 1972, Allen *et al* 1974).

6.2. Neutron transmutation doping

Naturally occurring silicon consists of three isotopes as shown in table 1. Each isotope can capture a thermal neutron so that it transforms into the next isotope of higher

Table 1. Absorption of thermal neutrons to produce transmutation doping of ^{30}Si to give ^{31}P . The total dose of neutrons must be restricted otherwise ^{31}P so generated is converted into ^{32}S which acts as a double donor in silicon with a deep level.

Isotopes	Abundance (%)	Thermal neutron absorption cross section (b atom $^{-1}$)	Relative absorption (%)	Reaction
^{28}Si	29.28	0.08	81.7	(n, γ) ^{29}Si
^{29}Si	4.67	0.27	14.0	(n, γ) ^{30}Si
^{30}Si	3.05	0.12	4.1	(n, γ) $^{31}\text{Si} \rightarrow ^{31}\text{P}$
^{31}P	—	0.09	—	(n, γ) $^{31}\text{P} \rightarrow ^{32}\text{S}$

mass. Of particular interest is the fact that ^{30}Si is converted into stable ^{31}P atoms which are just the usual group V impurities giving n-type conductivity (Jagannath *et al* 1981). Hence high-resistivity material (i.e. pure FZ crystals) can be uniformly doped with phosphorus if it is subjected to a uniform dose of thermal neutrons (Tannenbaum and Mills 1961), up to a typical dose of 10^{18} cm $^{-2}$. This technique has an advantage over chemical doping which leads to striations in the concentration of the phosphorus impurity. However, because of the irradiation, the crystal becomes damaged and is not suitable for the manufacture of devices unless the damage is first removed by a high-temperature anneal. The temperature required for this anneal depends upon the ratio of the fluxes of thermal neutrons to fast neutrons in the reactor. This ratio may be as high as 10^3 when anneals around 700 °C are satisfactory; as the flux ratio approaches 10^2 it is necessary to increase the anneal temperature to 900 °C because of the extra damage produced by the primary collisions of the fast neutrons. As it is desirable to keep the temperature as low as possible because of problems of metallic contamination (§ 4.2), the flux ratio should be as high as possible and heavy water reactors such as DIDO and PLUTO offer the best conditions. NTD has now become commercially viable (Janus and Malmros 1976) and, as an example, the throughput of silicon at AERE Harwell has been quoted recently to be at the level of 20 tonnes yr $^{-1}$ (Smith 1979). Excellent discrete devices are made from this material with superior characteristics to those made from chemically doped n-type silicon.

7. Diffusion at high temperatures

Self-diffusion in a metal occurs via a vacancy process with an activation energy E_D equal to the sum of the activation energies for formation of a vacancy E_f and migration

of a vacancy E_m (Simmons and Balluffi 1962). It was assumed by many workers that this process was also operative for silicon. Measurements of the self-diffusion coefficient have yielded values of $E_D \approx 5$ eV (Peart 1966, Fairfield and Masters 1967, Mayer *et al* 1977). It has been shown in § 5.2 that E_m for a vacancy is less than 0.5 eV so that E_t would have to exceed 4.5 eV. This leads to an estimated vacancy concentration at the melting temperature of only 10^{10} cm⁻³, many orders of magnitude smaller than the values measured for metals, and so the vacancy mechanism is open to question.

An alternative diffusion mechanism is via self-interstitials (figure 18). An interstitial moves through the lattice and can be thought to attach itself to some particular lattice atom, leading to the occupation of one lattice site by two atoms. This is the configuration demonstrated unambiguously by ESR measurements for boron and carbon impurity atoms in interstitial sites as discussed in § 5.2. The atom originally occupying the lattice site then slips into the adjacent interstitial site to form a dumbbell with the next substitutional atom so that this atom can subsequently diffuse away. Thus the original substitutional atom, which may be a radioactive species, moves a distance of one lattice spacing in the entire process and a mobile interstitial is still present in the lattice. This is the alternative process proposed by Seeger and Chik (1968).

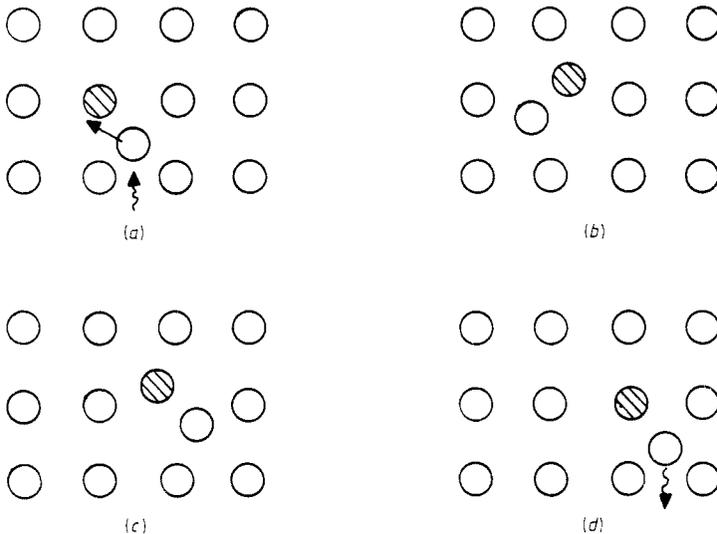


Figure 18. Diffusion by the interstitialcy process. We suppose the shaded atom in (a) is marked, perhaps as a radioactive species, and a silicon interstitial moves to an adjacent site. In (b) the two atoms form a dumbbell; in (c) there is a reorganisation so that the dumbbell moves along one lattice spacing. In (d) the dumbbell dissociates, leaving the radioactive atom in the site adjacent to its original position.

There is then the possibility that vacancies and self-interstitials are present in comparable concentrations, in which case two diffusion mechanisms are operative and there could be a change in the dominant mechanism around some particular temperature if the energies of formation of the two species differ. This model is advocated by Seeger and Chick (1968) and Seeger *et al* (1979) who claim that experimental data show a change in the slope of an Arrhenius plot for self-diffusion at about 900 °C. Not all workers agree that the evidence for this is convincing. An experimental difficulty is that radioactive silicon isotopes are not particularly suitable for such studies

because of low activities or short half-lives, and the diffusion measurements are limited to high temperatures and thin surface layers where non-equilibrium processes may occur. To overcome such objections it has been proposed that the diffusion of germanium in silicon might yield additional information because germanium has the same valence, a similar covalent size and suitable tracers are available. This led McVay and Ducharme (1975) to carry out studies which could be interpreted as supporting the view that an interstitial process occurred at high temperatures but that a vacancy process became more important at low temperatures.

Other processes have been investigated that might yield relevant information including gold diffusion at low temperatures, nickel precipitation on cooling heated samples, iron precipitation, the growth of stacking faults during oxidation of samples, the anomalous surface diffusion of phosphorus and the enhanced diffusion of other impurities near a heated surface. For recent overviews, the reader is referred to the papers of Seeger *et al* (1979) and Gösele *et al* (1981). A discussion of all these topics is outside the scope of this review, and would require the space of a separate article. Consequently we shall restrict further discussion to enhanced diffusion effects near a surface and its interpretation in terms of non-equilibrium concentrations of point defects.

Standard structures used in the manufacture of devices are those of sequential p-n-p or n-p-n layers produced by diffusion or epitaxial growth. Diffusion rates of the standard n- and p-type impurities, under conditions where surface oxidation occurs, show abnormalities and have led to expressions such as 'emitter dip', etc, by the manufacturers of transistors. Such effects have been known now for many years (see, for example, Lee and Willoughby 1972, Taniguchi *et al* 1980) and problems related to phosphorus diffusion have already been mentioned in §4.1. Recently, some particularly careful measurements have been reported which have been analysed in considerable detail (Hill 1981). We discuss these data first, which illustrate the existence of non-equilibrium defects, then the identification of the type (vacancy or interstitial) of defect present and finally try to make a connection with information found from irradiation studies.

The method used by Hill is shown in figures 19 and 20. The thin buried layer of silicon doped with boron is sandwiched between thicker layers of n-type material with the lower surface of the wafer protected by an inert layer of silicon nitride. Buried regions of silicon nitride are present to act as depth markers and interference microscopy was used to measure depths. The top surface of the structure has three regions labelled A, B and C; region A is again protected with silicon nitride, region B is simply coated with oxide and region C is exposed to the ambient. During heating, diffusion of the boron into the n-type material occurs as shown in figure 20, and was profiled by spreading resistance measurements. The expected Gaussian distributions were found from which it is a relative simple matter to extract values of the diffusion coefficient. Measurements made at 900, 1000, 1100 and 1200 °C allowed values of D_0 and E_D to be determined. Measured values of D were independent of the ambient during diffusion under region A, and were therefore ascribed to intrinsic diffusion D_i ; the values of D_i so obtained were in good agreement with previously published data. However, under regions B and C (figure 1) the rate of diffusion was significantly greater, except at the highest temperature when there was a reduction in D . Similar data were also obtained for phosphorus and arsenic diffusion into p-type silicon.

The conclusions may be summarised as follows. Diffusion under an oxidising surface at a temperature below 1200 °C leads to an enhanced diffusion coefficient

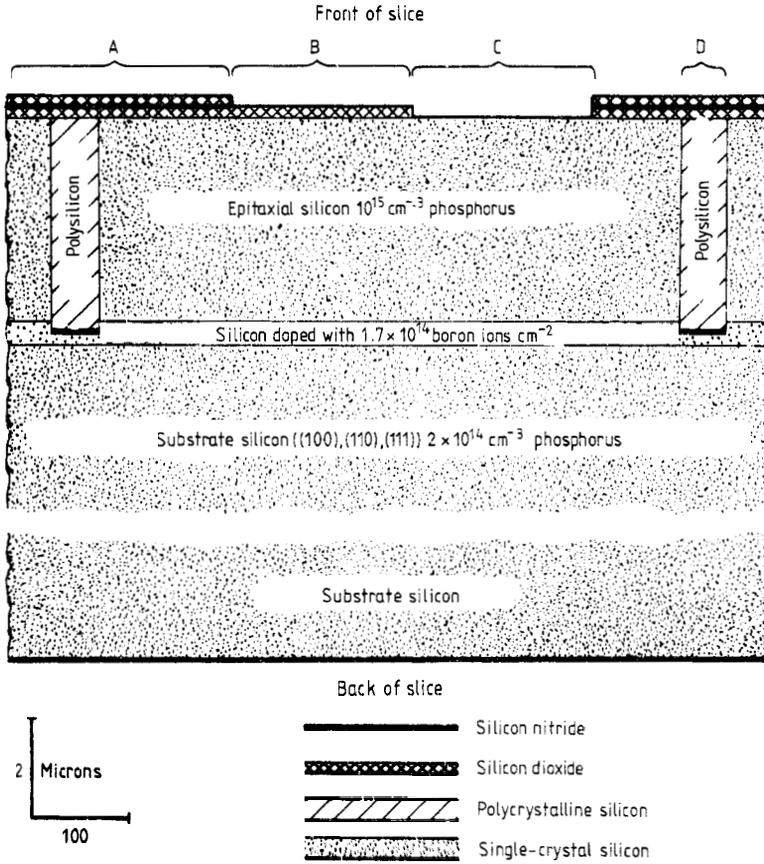


Figure 19. Schematic diagram of a vertical section through a marker layer structure. Vertical and horizontal scales are in a ratio 50:1 as shown (after Hill 1981).

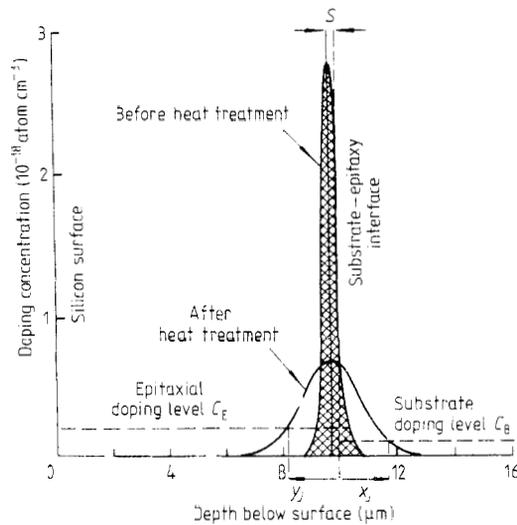


Figure 20. Dopant distributions and interface positions in marker structure before and after a typical heat treatment. Epitaxial and substrate doping levels are exaggerated for clarity (after Hill 1981).

with $\Delta D_{\text{ox}}(100) > \Delta D_{\text{ox}}(110) > \Delta D_{\text{ox}}(111)$, i.e. the process is dependent on the orientation of the surface plane of the silicon. It was shown experimentally that this was not due to anisotropic diffusion, which cannot occur in a cubic crystal for reasons of symmetry, but rather to different kinetics of the oxidation process at the surface. The increase in diffusion coefficient ΔD_{ox} , defined as $D_{\text{ox}} = D_i + \Delta D_{\text{ox}}$, was found to have an activation energy of 2.31 ± 0.08 eV, essentially independent of the dopant in the buried layer and the slice orientation. It is interesting to note that this value is very close to that found for the diffusion of oxygen of $E_D = 2.6 \pm 0.15$ eV (see Peart and Newman 1973), although Hill makes no mention of this coincidence. Neither does Hill comment on the nature of the non-equilibrium defects generated at the surface which lead to the enhanced diffusion of boron, phosphorus and arsenic.

There are two pieces of information which indicate that it is self-interstitials that are generated predominantly at a silicon surface during oxidation. Clearly an excess of such defects may lead to their aggregation and eventual collapse into planar stacking faults. The theory of image formation in electron microscopy allows the nature of dislocation loops to be determined experimentally, according to the observed contrast (see Seeger *et al* 1979). Consequently it is possible to be certain whether, in a given loop, there is an extra sheet of atoms (interstitials) or a missing plane of atoms (condensed vacancies). Measurements for oxidation-induced stacking faults (OSF, see § 3.1) show that the interstitial model is correct and that the interstitials concerned are self-interstitials and not oxygen impurities (Mararka and Quintana 1977, Leroy 1979). The rate of increase in the peripheral length of the loops gives a measure of the rate of deposition of the interstitials and is found to be temperature-dependent with an activation energy of 2.4 ± 0.1 eV for $T < 1200$ °C. In addition, the growth rate is dependent on the surface orientation of the wafer in the sequence (100), (110), (111), with (100) giving the highest rate. Finally for $T > 1200$ °C there is shrinkage of pre-existing loops with a much higher activation energy. The evidence is overwhelming that the process leading to the enhanced diffusion of the impurities in the work of Hill is the same as that leading to the growth of the stacking faults. The conclusion is that self-interstitials are generated at the surface of the silicon in a concentration above the equilibrium value for $T < 1200$ °C (see also Wada and Inoue 1981).

Further evidence for interstitial injection is afforded by the work of Strunk *et al* (1979) who showed that the interpretation of some earlier measurements was in error. There may be pre-existing dislocations in the region of non-equilibrium defect generation under the oxidising surface. As a result of climb, a straight screw dislocation is converted into a helix. A given sense of the helix would indicate absorption of interstitials or emission of vacancies; the other sense would give the other two possibilities (see also Seeger *et al* 1979). The experimental result leads to the first conclusion. Since it is known from the *enhanced* diffusion that excess defects are present it follows that the dislocations must be absorbing interstitials. This result affords further evidence that oxygen precipitation is not the cause of the climb.

The overall conclusion would be that boron, phosphorus and arsenic all diffuse via an interstitial process. This result would not come as a surprise for boron impurities as strong interactions with self-interstitials were found in irradiated samples. However, for the group V donors, it has been assumed that a vacancy diffusion process was operative (Yoshida 1981). In addition, we are unaware of any ESR data that indicate simple interactions of interstitials with phosphorus or other group V impurities (such an interaction was, however, suggested by Sieverts and Ammerlaan (1977) as a

possibility to be explored). A possible explanation is that there is co-generation of vacancies and interstitials at the oxidising surface with excess interstitials (see Gösele *et al* 1981). It would appear that further work is still required to reach a satisfactory conclusion.

8. Conclusions and discussion

We started the article with a brief history of the development of silicon followed by an account of the methods used to manufacture single crystals. Molten or gaseous silicon compounds have to be contained in other materials, and during processing at high temperatures there is mixing with gases such as hydrogen which may themselves be impure. The conversion of polycrystalline silicon to single-crystal form is another high-temperature process involving apparatus with moving mechanical parts, blocks of carbon and the use of a crucible of silica for pulled CZ crystals. Inevitably, there is chemical contamination from oxygen, carbon, nitrogen, residual boron and other elements from silica crucibles, metals, perhaps hydrogen, etc. We indicated that impurities were not uniformly distributed but were present in swirl patterns. Yet a further complication arises from the condensation of supersaturated intrinsic defects as the crystal cools to room temperature. Such clustered defects act as nucleation centres for impurity precipitation which in turn can lead to the generation of further defects, because of the build-up of large internal stresses. Slices of such silicon have to be cut, etched and polished and have to survive other 'preliminary' treatments which may introduce further contamination, point defects or even dislocations. The resulting material is clearly not homogeneous, chemically pure or structurally perfect. But this is real silicon from which devices are made and which is used for experimental studies by solid-state physicists who frequently compound the problems by not taking adequate care to minimise further contamination or defect generation.

We identified oxygen as perhaps the most important impurity apart from those used to control the electron or hole concentration. We have been 'aware' of oxygen now for some 25 years but are still very ignorant in many respects. In a recent review paper Patel (1981) commented that after all this time we still do not have reliable data for the solubility and diffusion coefficient of oxygen in silicon. Neither do we know how oxygen atoms start to cluster during heat treatments at either low temperatures (450 °C) or high temperatures (1000 °C), in spite of the wide range of physical techniques brought to bear on these problems. Small clusters of oxygen act as double donors (see the recent review of the literature by Kimmerling and Benton (1981)) but we do not know why and the sequential growth of precipitates as an atomistic process is not resolved.

Carbon impurities influence the behaviour of oxygen and other processes, and can also become 'lost' in crystals in unknown configurations. Boron is usually present in a low concentration in undoped crystals, and nitrogen may be, but nothing is known about the possible role these impurities may have in the nucleation of oxygen precipitates. If 'small' carbon atoms are considered to be important in this context, one may ask why not small boron atoms?

Our understanding of metallic contamination during high-temperature processing is not at all well understood because various interactions lead to the formation of complexes. Much early work needs to be repeated with the heat treatment of samples carried out under 'clean' conditions.

The interesting areas of radiation damage are now moving towards correlating energy levels (DLTS data) with structural information (mainly ESR data) and there are some exciting developments of a fundamental nature. Much has been learned about vacancies and interstitials and their interactions with a wide range of impurities, but there is an on-going challenge to relate this information to processes occurring in the diffusion regime at high temperatures. Specifically, we should like to know whether vacancies or self-interstitials are dominant or whether both defects are present together under equilibrium conditions.

As a final comment, one could predict that as device technology drives towards ever smaller dimensions, further practical problems will arise which in turn will throw up challenges at the level of fundamental understanding. In other words, there is every reason to think that the invaluable partnership established between technology and basic solid-state physics will continue for a further indefinite period.

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