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Impurity ion implantation into silicon single crystals: efficiency and radiation damage

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Contents

Abstract. The ion implantation method is analysed from the point of view of its efficiency as a technique for doping silicon with donor and acceptor impurities, for synthesising silicon-based compounds and for producing gettering layers and optoelectronic structures. The introduction, agglomeration, and annealing of radiation-produced defects in ion-implanted silicon are considered. The role of interstitial defects in radiation-related defect formation is estimated. Mechanisms of athermal migration of silicon atoms in the silicon lattice are analysed.

1. Introduction

In the second half of the 20th century silicon, one of the most abundant elements in the Earth's crust, has become — and is most likely to remain — the most widely used and the cheapest among solid state electronics materials. American economists estimate that by the early 21st century the production of silicon semiconductor devices in the USA may be about as lucrative as the car industry.

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The development of solid state electronics in the last 15 years has been dominated by 'planar' systems which came to take over from the three-dimensional structures of germanium — and later silicon — devices. The method of major importance to planar design has been the implantation of the accelerated ions of electrically active impurities, something which first appeared to be an exotic, over-complicated and unnecessarily expensive venture.

The advantages and natural limitations of the ion implantation technique have been discussed in Ref. [1], and also by one of us (VSV) in a 1985 UFN review article [2]. In recent years, the body of relevant information has grown considerably. The present review is deliberately limited to data on single crystal silicon; the inclusion of amorphous and 'porous' silicon appears impossible within a standard-length UFN paper. Besides it seems premature to address these questions.

Because of the paramount importance of silicon as material number one in solid state electronics, problems related to the growth of single crystals and to their imperfections have been the subject of numerous publications, international conference proceedings, and monographs, in particular [3 – 5]. There is no doubt that our knowledge in this area will advance from year to year.

Within our topic, the question we address is: to what extent is a tour de force, nonequilibrium method like fast-ion implantation effective as a means of controlling silicon properties? There was considerable doubt repeatedly voiced by authorities that the crystal region near the end of the track of the implanted ion, containing clusters of many (typically several hundreds) displaced atoms, would be able to recover properly.

However, it was shown experimentally long ago that the electrical activity of standard dopants such as phosphorus

and boron, when introduced by ion implantation, may be very high although — for reasons to be discussed further on — often somewhat lower than for most of the Group III and V chemical impurities which are introduced into silicon under quasi-equilibrium crystal growth conditions. In the latter case, impurities forming hydrogen-like centres have about 100% activity, provided their concentration is not above the solubility limit.

The advantages of ion implantation as a technique for the precision local doping of solids are currently well known to specialists. These are, above all, high reproducibility and the possibility of introducing any type of impurity into the material (silicon, in our case).

In recent years great strides have been made in accelerator design technology. A tenfold increase in ion beam current density has been achieved and effective methods for removing heat from the target developed; the latter was a well known obstacle to early microelectronics applications of ion implantation because of the often uneconomical exposure times required.

Accelerators for working with heavy ions of up to tens of MeV have been built which make it possible (via synthesis of SiO_2 or Si_3N_4 at the required depth) to produce isolating layers with which to separate the active region, where transistors, diodes, and other integrated circuit 'microelements' are located, from the passive substrate intended to release heat. The main complication we hinted at above is that the radiation-produced defects which are unavoidably present immediately after the ion implantation require that some type of influence be exerted on the resulting structure in order to translate it from the initial highly nonequilibrium (metastable) state into a new state closer to equilibrium. This process is usually called annealing [1, 2].

2. The spatial distribution of implanted ions

The loss of energy by charged particles in interaction with condensed media has been treated in many works, notably in the remarkable monograph by Niels Bohr [6]. Since then, approximate methods for calculating the energy losses of heavy charged particles have been improved greatly. A detailed exposition of the methods is given in the book by Kumakhov and Komarov [7] and in the tables of Ref. [8].

One of the effects that exert an appreciable influence on the final depth distribution of implanted ions is channeling, the anomalously deep penetration of some ions along natural 'channels,' i.e. the crystallographic (usually small-index) axes. This effect is especially important for silicon single crystals because of their high perfection.

It has been shown by direct experiment that along with channeling (which proceeds under conditions of optimal single crystal orientation), there unavoidably exists random channeling involving some portion of the fast ions: those that did not enter the single crystal at an easy penetration angle initially.

In the absence of channeling, present-day range calculation methods (see Refs [7, 8]) agree with experiment to within ±10%. In the literature on range calculation one usually employs the term 'amorphous silicon', and this should be regarded with caution since genuine amorphous silicon differs in density from its single crystal counterpart.

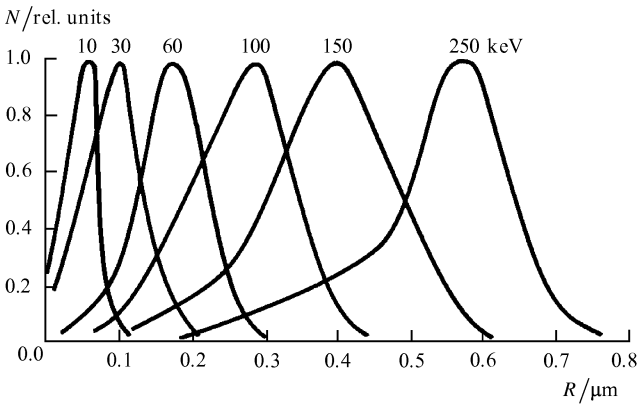

Figure 1. The most probable values and scatter of boron ion ranges in silicon with no channeling [7].

It would be better to speak of an absence of channeling directions.

Fig. 1 presents data on the most probable values and scatter of the range lengths of boron and silicon ions, in the absence of channeling, for ion energy intervals most typical of implantation accelerators now in large batch production in the USA, Japan, and other countries.

In Fig. 2 we demonstrate the influence of channeling on the distribution profile of phosphorus ions implanted into a perfect silicon single crystal, and into a silicon crystal preliminarily amorphised with silicon ions [9].

Fig. 3 reproduces the dependence of the average range of ions on their mass in silicon, and also shows the scatter in range due to the statistical nature of the processes

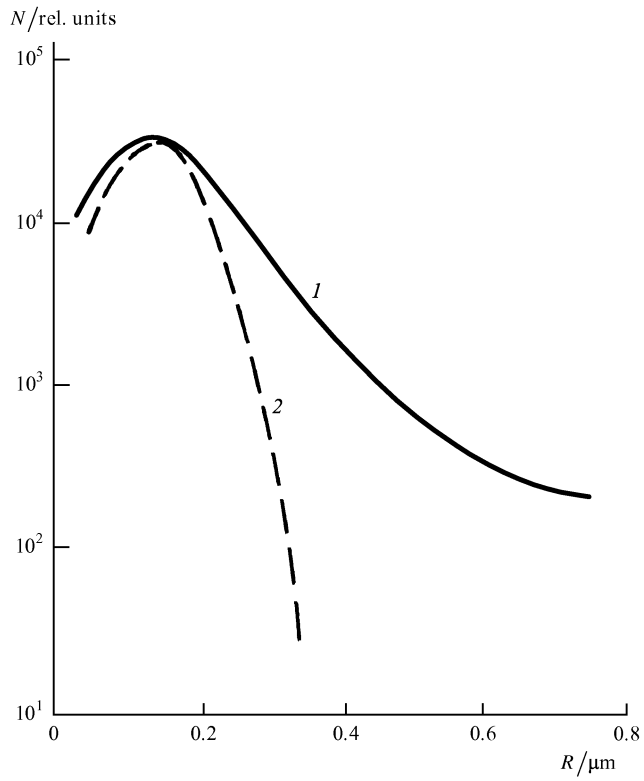

Figure 2. Effects of channeling on the distribution profile of phosphorus ions implanted (*1*) into a perfect single crystal of silicon, and (*2*) into a crystal first amorphised with silicon ions [9].

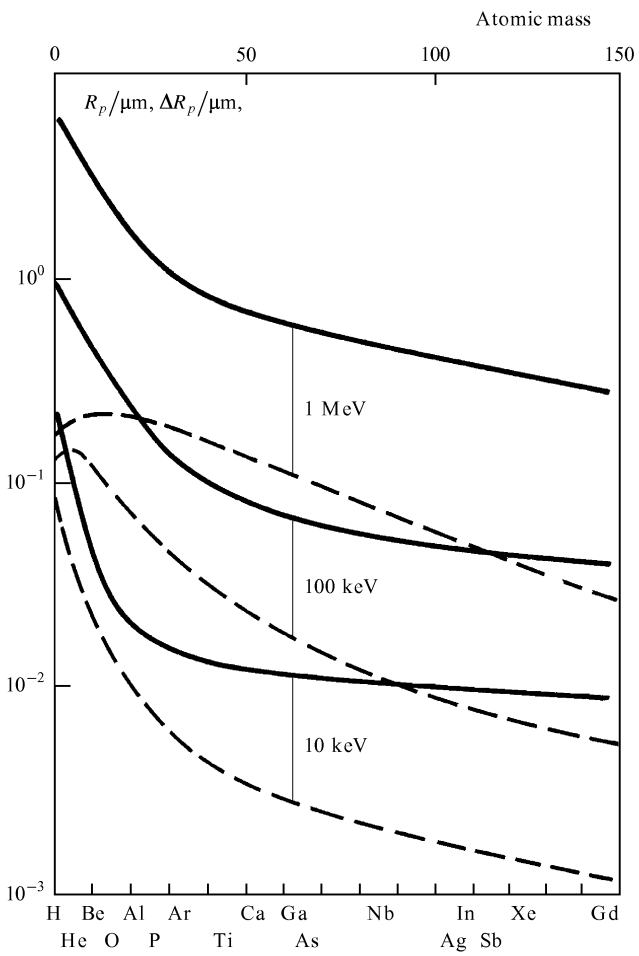

Figure 3. Mean values and scatter of ions of various masses in silicon in the absence of channeling [2].

responsible for the gradual decrease in the kinetic energy of ions deep in the target. Although energies above 1 MeV or so are used very rarely because of the significant development and maintenance expenditures required by heavy ion accelerators, work in this direction is being done systematically in some laboratories. The future promises an intensification of this line of research, primarily on protons, with the intention of producing very deep layers of semi-insulating silicon whose conductivity is reduced to a minimum ($\rho = 2 \times 10^5$ Ω cm and more) by introducing deep-level radiation-induced defects.

A method is currently being developed for producing isolating SiO_2 (and Si_3N_4) layers sufficiently deep for problems in silicon microelectronics to be resolved. Unfortunately, the doses one needs for the $Si-SiO_2$ (or $Si-Si_3N_4$) phase transitions to occur are quite high and require long irradiation times. Although modern ion beam focusing techniques do allow large current densities, long-term irradiation is necessitated by the heat removal requirement: otherwise, strong heating and the modification of material properties, or even the melting of the target, are unavoidable.

It should be noted that, apart from the shallow Group III and V donor and acceptor impurities, implanting rare earth and in particular erbium ions is of increasing interest for the solution of optoelectronics problems now on the agenda. To the so-called intra-central radiative transitions in the 4*f* shell of erbium there corresponds a system of narrow luminescent bands at about a 1.54 μm wavelength. This radiation is apparently independent of the nearest lattice environment.

Michel and Kimmerling with coworkers [10] have shown that high-energy (5 MeV) erbium ion implantation followed by prolonged annealing of the silicon lead to the appearance of about 1.5 μm deep stable luminescence centres which the authors of that work associate with clusters of atomic erbium resulting from the fall-out of a second phase. Erbium-implanted silicon not only exhibits photoluminescence but, when in p–n junction structures, also shows injection luminescence, which enabled the authors to fabricate light-emitting diodes of a type which proved to be very interesting for optoelectronics technologists.

Most recently, considerable progress in the development of multiple-ion sources permitted a substantial increase in ion range to be achieved. A recent paper by Biersack [11] provides an analysis of the passage of multiply charged ions through materials and presents a comparison with available data for silicon.

3. Initial positions and activation of implanted impurity atoms

From numerous publications starting from the early work of the Gusevs [12, 13] it is evident that the initial position of an impurity atom in silicon should be considered as taken at random from the following options:

(a) the impurity substitutes a silicon atom in the lattice in its initial structure;

(b) the impurity comes to a stop at one of the possible interstitial positions;

(c) the impurity forms an associate (complex) with one or more point defects; or

(d) the impurity stops within the amorphous region into which the initial silicon has transformed (limiting case).

A detailed analysis of the cases (a) and (b) is given below. However, the major objective of ion implantation research has most often been to maximise the electrical activity of the implant, which, for the Group III and V elements, implies the substitution of a silicon atom. Therefore, even in early work the ion implantation procedure was followed by annealing under quasistationary conditions, i.e. by long-term heating in a furnace.

It is appropriate to recall here that this very natural technique was first used back in the 1950s by Lark–Horovitz to minimise the effect of irradiation-produced defects on germanium. The irradiation of the latter (by neutrons) was aimed at obtaining impurities as a result of the nuclear reactions involved [14].

In the case of silicon, prolonged annealing almost always has unpredictable side effects due to the diffusion of uncontrollable impurities throughout the crystal. As is known, silicon single crystals unavoidably have appreciable concentrations of carbon, nitrogen, and oxygen [3, 4]. A brief discussion of this question is also given in Ref. [5].

Smirnov, Khaibullin and colleagues [15] were first to propose and implement the method of local pulsed annealing of ion implanted semiconductors, above all of silicon. The technique they employed first in their experiments was local excitation by pulsed laser radiation. (The term 'laser annealing' is still in use, although it is more appropriate to speak of the 'local pulsed annealing of implanted structures').

After numerous and successful applications of this technique to silicon it turned out that pulsed excitation by incoherent light or by fast electrons give similar results.

Over several years, discussions were held, theoretical estimates made, and experiments carried out in order to find out whether the situation is dominated by the short-duration thermal excitation of the silicon lattice or alternatively by the internal ionisation effect, i.e. the massive generation of pairs of nonequilibrium charge carriers in the near-surface layer.

In fact, it was established back in the 1960s that the charge state of point defects in silicon greatly influences their mobility and stability properties [5, 16]. This fact is presently beyond any doubt and invariably employed in interpreting phenomena associated with the appearance of 'secondary' defects (see below). Direct experiments have shown, however, that in the case of silicon, pulsed annealing results from the short-duration heating of the near-surface layer and that ionisation processes play only a secondary role [15].

As noted earlier, Group III or V impurities substituting host atoms in implanted silicon ultimately have the same energy levels and the same charge-carrier capture cross sections as the impurities introduced by the single-crystal or epitaxial-film growth processes. However, because of relatively stable residual defects of radiative origin, the ion implantation method is, with a few exceptions, less effective.

On the other hand, some experiments suggest that sometimes a proper choice of an impurity dose and a pulsed annealing regime may yield a high level of impurity supersaturation and the implanted region will have electrically active impurities in concentrations one or more orders of magnitude larger than the equilibrium solubility value. The stability of such structures has not yet been studied in detail.

Apart from implanting shallow donor and acceptor impurities in order to produce planar electronics structures, in some cases the implantation of other ions (in particular, of the transition elements or inert gases) has been valuable for the creation of luminescence centres. Moreover, it has been found fairly recently that implanting silicon with rare-earth ions produces 'gettering' of point defects and of uncontrollable impurities, which even at low temperatures migrate from the 'working' portions of the silicon plate (where active elements such as diodes and transistors are made) into its nonactive region (for example, into the near-surface layer at the other side of the plate).

The mechanism of gettering is not yet completely understood, but most likely is due to the development of large mechanical stresses within and outside the implanted layer.

4. Primary radiation effects and their complexes with impurity atoms

Many of those authors dealing with the radiation resistance of silicon and silicon-based devices rely in their estimates on the notion of the cascade multiplication of primary Frenkel pairs that form in collision processes: an idea known from the work of Dienes and Vineyard [17].

There is an important point to note here. The threshold energy for a collision event to displace an atom from its site does not of course correspond to a zero-to-unity step for the displacement probability but is a smoother dependence. Therefore, taking into account the anticipated annihilation instability of 'close Frenkel pairs', such estimates should rather be viewed as giving the maximum limiting number of Frenkel pairs.

Nevertheless, it is these estimates which are most often used in predicting the radiation resistance of a semiconducting material [16]. This is analogous to introducing a safety factor when designing bridges or the running-gear car parts. The term DPA (displacements per atom) has come into prominent use in the literature.

Brinkman [18] proposed an alternative view of the defect formation process for the case when a fast particle loses a large amount of energy at the end of its range. According to his estimates, the average distance between collisions that produce secondary atoms approaches the interatomic separation even if the energy of the primary atom is of order 2×10^4 eV. The primary atom is decelerated extremely rapidly, thus creating a dense region of secondary displacements. Brinkman argues that within this region it is impossible to consider each displacement (or Frenkel pair) separately because atoms in the region of maximum energy release transform into a completely disordered melt-like state.

According to Ref. [18], near the end of the track of the initial atom (an ion in the silicon lattice in our case) inversion takes place, i. e. some of the atoms initially near the track are ejected a maximum distance away. The disordered region recrystallises within $10^{-10}-10^{-12}$ s, starting from the outer boundary. It is assumed that most of the atoms will rearrange themselves into the initial lattice.

Unfortunately, no quantitative estimates are possible with the Brinkman model. The model has been criticised by Seitz and Koehler [19]. Brinkman's qualitative argument deserves serious attention, however.

At present, the formation of large clusters of defects at the end of the ion track in implanted silicon (and other semiconductors as well) is invariably discussed in terms of the cascade model.

Along with the collision-assisted displacement of silicon atoms from their sites, there is the Frenkel pair formation due to processes induced by the excitation of the elec- tron subsystem of the crystal [20]. The mechanism and efficiency of such processes still remain the subject of discussion.

According to one model, Frenkel pair formation is initiated by the multiple ionisation of silicon atoms. An alternative mechanism, proposed by Karpov and Klinger [21], assumes that in the initial (in our case, silicon) crystal there are 'preferred pairs' containing a silicon atom and an impurity ion interacting with one another. As far as silicon single crystals are concerned, which of the above mechanisms is more effective is not clear at present.

Based on the models above it is estimated that the number of primary Frenkel pairs due to such processes may increase by 30 – 50% from its initial value (according to Ref. [21], in highly doped silicon the contribution of the 'impurity' mechanism should be greater). The 'fate' of vacancies and interstitials following Frenkel pair generation is also strongly dependent on the presence of chemical impurities in the crystal.

It has been convincingly demonstrated that isolated vacancies and interstitials in silicon are mobile even at low temperatures. It is also known that isolated silicon interstitials at room temperature and above do not behave

as electrically active centres. (In the simplest model they could act as shallow donors). Other effects associated with host interstitials will be addressed below.

The behaviour of the members of Frenkel pairs in silicon is illustrated in the 1993 paper of Watkins [22] (Fig. 4). The figure shows the important role of impurities in irradiated silicon. The same diagram shows the energy levels of vacancies in different charge states. Microscopic models of complexes formed by vacancies combining with one another and with chemical impurities are given in Ref. [5].

Fig. 5 shows the temperature ranges where vacancy-impurity complexes exist. Many of these have deep energy levels and affect significantly the electrical conductivity and recombination processes in crystals subjected to implantation and subsequently annealed.

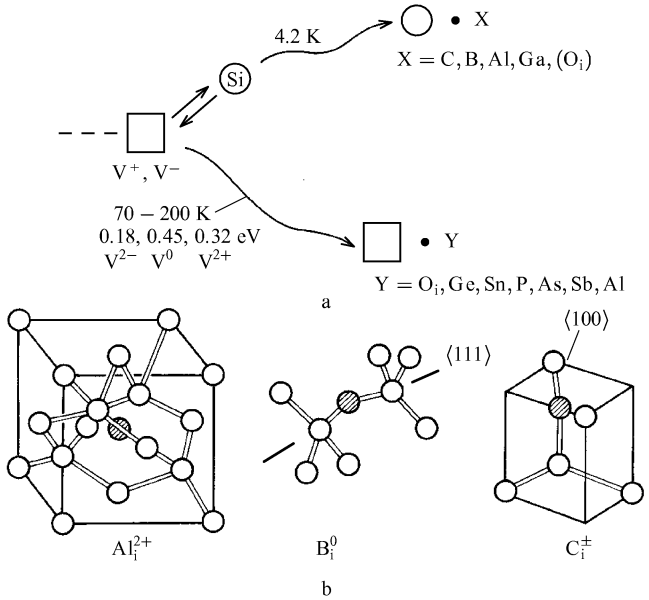

Figure 4. (a) Migration processes and the interaction between the members of Frenkel pairs in silicon [22]. (b) Complexes of interstitial silicon atoms trapped by substitutional aluminium, boron, or carbon atoms as obtained from the EPR spectra [22].

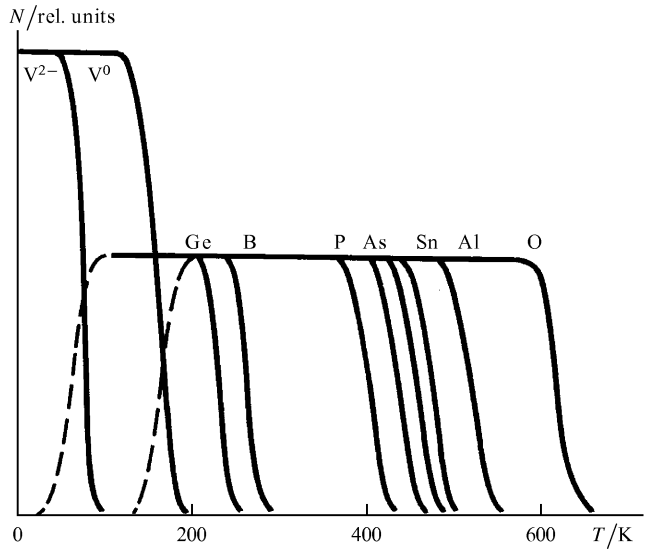

Figure 5. Temperature ranges of existence of basic vacancy–impurity complexes [5].

5. Divacancies and polyvacancy complexes

Divacancies may form as primary defects if the incident particle transmits energy sufficient to displace two neighbouring silicon atoms. The increase in the number of divacancies observed experimentally in the vacancy-annealing temperature range suggests that divacancies also appear as two isolated vacancies agglomerate.

Models of spatial divacancy configurations, together with the corresponding energy levels, are given in Refs [5, 16]. Boron, carbon and oxygen atoms can capture silicon interstitials, thus reducing annihilation processes and facilitating vacancy agglomeration.

Ion implantation, as well as fast-neutron irradiation, also leads to polyvacancy complexes of three, four, five or more neighbouring vacancies [16]. Fig. 6 shows the temperature ranges where single vacancies, divacancies, and polyvacancy complexes exist.

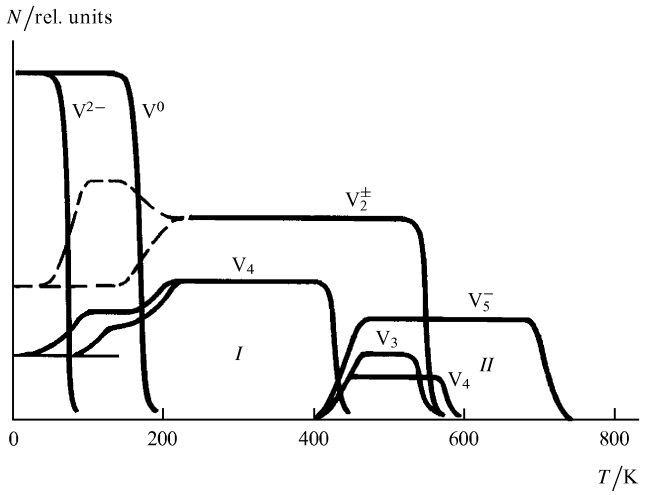

Figure 6. Temperature ranges of existence of single vacancies, divacancies, and of polyvacancy complexes [5]; *I* — planar complex, *II* — nonplanar complex.

6. Processes involving point defect clusters during the ion implantation of silicon

As noted earlier, an ion-implanted silicon single crystal is a spatially heterogeneous system which includes clusters located near the stoppage point of implanted ions, and point defects (such as divacancies and complexes of vacancies with chemical impurities) distributed more or less randomly over the volume. These defects are mainly distributed within the implanted ion's range below the surface. Clusters are concentrated at depths roughly corresponding to the most probable projection of the range onto the initial ion direction.

Apart from random channeling [7], which leads to the deep penetration of both ions themselves and defects they produce, it has been found recently that some defects penetrate abnormally large distances compared to the ion range. This phenomenon, not altogether properly termed the 'long range effect', has been observed in silicon and in other semiconductors, in particular GaAs [23].

The nature of the long range effect remains unclear. Some ascribe it to the large mechanical stresses arising in the region of the maximum concentration of implanted impurities: the propagation of the stress region gives rise to additional defects, strictly of nonradiation origin. Others associate this effect with shock waves propagating around the clusters formed in the crystal [24].

The body of experimental results have led to the notion of irradiation-assisted defect formation in heavy-particle irradiated silicon (see Ref. [24] for a discussion). Given the high mobility of interstitial atoms, they were assumed to disperse in a very short time from the formation point to sinks. The defect cluster then remains with single vacancies alone. These are also mobile and participate in the formation of complexes such as divacancies or impurity-containing complexes.

For small primary clusters with low vacancy concentration, it is expected that the vacancies will disperse giving rise to secondary stable defects primarily outside the initial displacement cascade ('runaway' primary cluster). If the size of the cluster and the concentration of vacancies in it are sufficiently high, the formation of stable complexes (mainly divacancies) will occur primarily in the volume of the primary cascade ('congealing' cluster).

This picture remains generally accepted. However, Watkins [26], studying defect formation in silicon irradiated at low temperatures by 46 MeV electrons (which characteristically initiate displacement cascade formation), found that divacancies form as primary defects and that their concentration does not increase on further warming to room temperature. The divacancy concentration was about 5% of that of the single vacancies.

Now what is the difference between the displacement cascades that form in silicon irradiated by high energy (46 MeV) electrons and those resulting from neutron or ion irradiation? First of all, the higher local density of atomic displacements in the latter case. But if vacancies form primarily in cascades of lower displacement density, then it is expected that at higher densities the efficiency of their introduction will not be less. Moreover, divacancies as primary defects also form under light-particle irradiation, when cascades do not appear, i.e. when only isolated point defects form [27, 28].

For a high local density of defects in a cascade, one expects that the divacancies that form as primary defects do not manifest their individual properties. A divacancy as a specific centre having its own structure — and, more important, its own energy states — can be only considered against the background of a perfect crystal lattice.

As a consequence of the elastic distortions of the lattice due to the defects surrounding a divacancy — predominantly due to single vacancies, whose concentration is about 20 times higher — the divacancy loses its individuality. Upon annealing the vacancies, the crystal matrix becomes more perfect, and divacancies do not form any more but just manifest themselves. Concentration effects will be addressed again in Section 7.

Let us here discuss the well known experiments on divacancy afterformation [29, 30]. The increase in divacancy concentration in silicon upon low-temperature neutron or ion irradiation was obtained by raising the temperature in parallel with low-energy electron illumination. The process started at 60 K. The divacancy concentration reached the same values as with no illumination. The results were interpreted as divacancy afterformation.

The decrease in the temperature of the process was ascribed to the higher mobility of vacancies when in the negative charge state. One hardly expects, however, that the afterformation of divacancies from neutral and negatively charged vacancies will be equally effective, because of the electrostatic interaction between vacancies in the latter case. In our view, this experiment does not substantiate the fact of divacancy afterformation but rather casts a shadow of doubt on the mechanism discussed.

7. Radiation-produced defects in silicon bombarded by heavy particles

Radiation damage in silicon is mostly studied by methods which monitor particular types of local centres. Interpretation in most cases is based on the analysis of EPR spectra. Optical methods like IR absorption and luminescence are widely used. Piezospectroscopic absorption and luminescence studies give insight into the symmetry properties of point defect centres.

The agglomeration of prevailing vacancy defects, i.e. of divacancies, has been examined by EPR [31] and IR absorption [32, 33]. In Fig. 7 we have used EPR data to show the change in the concentration of divacancies in the negative charge state in silicon layers radiated by different doses of O^+ ions. Shown also is the agglomeration of tetravacancies (Si – P3 centres) [34] as well as of the centres of amorphous phase (in EPR spectra, an isotropic line with a g factor of 2.0055).

As the dose of O^+ ions increases, the concentrations of both divacancies and tetravacancies reach a maximum and then start to decline. The decline has nothing to do with silicon amorphisation, however. The amorphisation starts at much higher irradiation doses. A similar picture of the agglomeration of divacancies in the negative charge state during the irradiation of silicon with various types of ions was observed with IR absorption using the 1.8 μm band [32, 33].

The decrease in the concentrations of divacancies and tetravacancies is due to concentration-related self-suppression of specific properties of the defects. A highly damaged

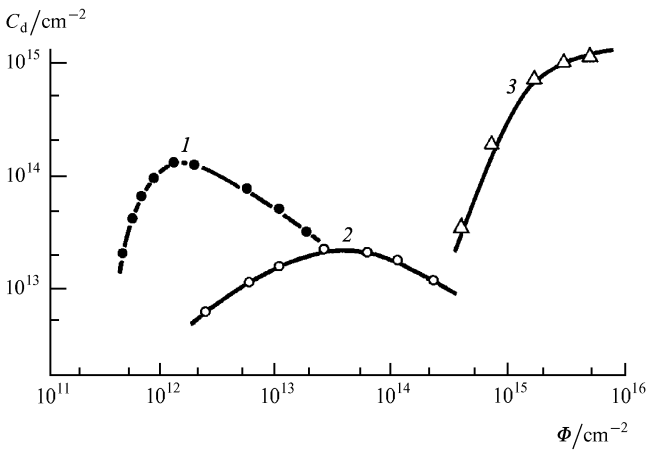

Figure 7. Variation of the concentration of divacancies (*1*), tetravacancies (*2*), and of the centres of amorphous phase (*3*) in silicon versus O^+ ion dose [31].

region in which point defects lose their individual properties while conserving crystal structure is called CDR, for crystalline defect region [33]. Ref. [32] yields an estimate of 10^{20} cm^{-3} for the limiting concentration of divacancies in clusters in which the divacancies still manifest their individual properties.

For silicon irradiated with reactor neutrons, IR absorption data [35] suggest a divacancy concentration of 10^{19} cm^{-3} for primary clusters (i.e. for those formed in one displacement cascade). This value characterises the average concentration of defects over the cluster. At the centre of a cluster their concentration is markedly higher.

The same is true for silicon implanted with ions of intermediate mass with energies of the order of 100 keV. Noting that the concentration of the produced vacancies is about 20 times that of divacancies, it seems reasonable to blame concentration effects on the lack of observability of divacancies in neutron-irradiated or ion-irradiated silicon at low temperatures.

8. Studies of radiation-produced defects in silicon using integral methods

It can be seen from Fig. 7 that differential methods (i.e., ones monitoring specific types of defect centres) lead to a lack of information on the agglomeration of radiation damage between the points where the concentration of point defects starts to fall and where amorphisation begins. In this case, methods investigating the overall distortion of the crystal may be of use.

Among the integral methods, optical reflection, x-ray diffraction, and ion backscattering appear to be the most weighty from the point of view of the volume of the studies performed and results obtained. Ion backscattering is particularly informative in the channeling regime. It enables one not only to determine the integral degree of crystal distortion but also the localisation of impurity atoms. It is this latter point which is the main advantage of the method.

In determining the overall distortion of the crystal, x-ray diffraction methods are much more sensitive than the ion backscattering technique. By studying the interference of x-rays diffracted on the implanted layer, radiation-damage depth distribution profiles can be constructed without destroying the implantation layer [36–38].

The fundamental parameter of a crystal is its lattice period. It is sensitive to impurity doping and to radiation-related defects. The lattice period may be measured with a minimal error of 10^{-8} Å [39], but the bulk of x-ray diffraction studies have been made with an error of 10^{-5}–10^{-6} Å.

When under reactor neutron irradiation, the silicon lattice period increases isotropically. In implanted layers its change is along the normal to the implantation plane, because in the plane the layer is bound rigidly to the substrate. As amorphisation starts, the break-up of interatomic bonds and relaxation of elastic stresses take place [40].

Fig. 8a shows the variation of the lattice period in a silicon layer, Δa, with the dose Φ of Si^+ [41]. The curve *1* represents the agglomeration of intrinsic radiation defects. (Curves *2–4* are discussed in Section 10). Up to a Si^+ dose of 1×10^{14} cm^{-2}, where isolated regions of defect clusters are introduced, the $\Delta a(\Phi)$ dependence is linear. The

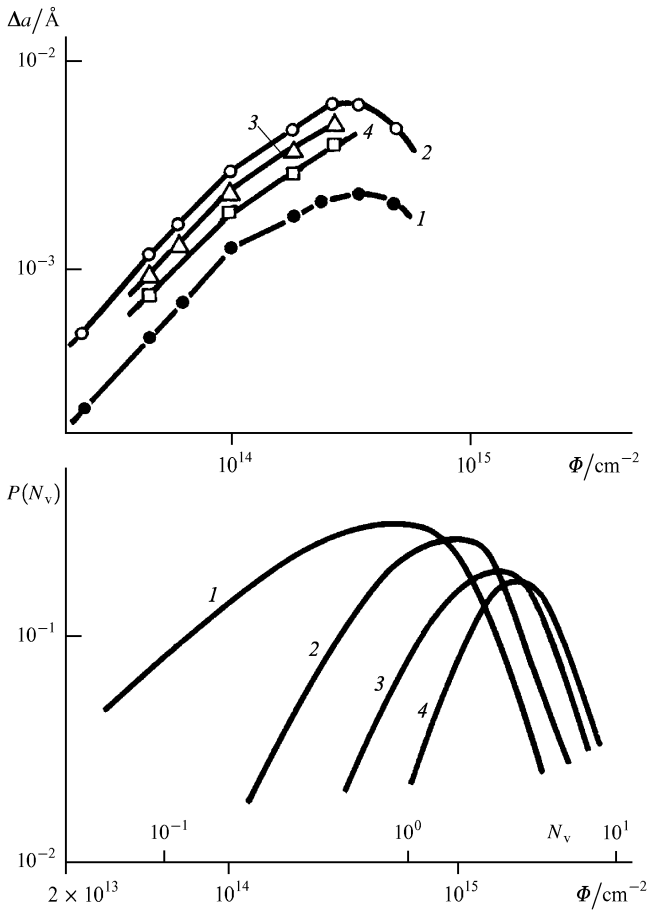

Figure 8. (a) Lattice period changes in silicon with Si ion implantation (*1*) and with preliminary Sb, As, and P doping (*2–4*) [41]: (*1*) Si (B), $\rho_0 = 10\ \Omega$ cm; (*2*) $\Phi_{Sb} = 2 \times 10^{14}$ cm^{-2}; (*3*) $\Phi_{As} = 1 \times 10^{14}$ cm^{-2}; (*4*) $\Phi_P = 2 \times 10^{14}$ cm^{-2}. (b) Distribution of relative volumes occupied by non-overlapping (*1*) and *n* times overlapped (*2–4*) defect clusters.

sublinear character of $\Delta a(\Phi)$ for Si^+ doses above 1×10^{14} cm^{-2} is due to the fact that the defect annihilation increases as displacement cascades overlap with defect clusters introduced earlier. The relaxation of elastic stresses in the beginning of the amorphisation process at the ion dose of 6×10^{14} cm^{-2} manifests itself as a bend in the $\Delta a(\Phi)$ curve.

Fig. 8b represents the relative volume distributions for defect clusters which do not overlap (curve *1*), overlap twice (curve *2*), etc. The distributions are described by the Poisson probabilities. For Si^+ ion implanted silicon, the limiting defect concentration corresponding to the transition of the material to the amorphous state is achieved at the triple overlap between defect clusters, and in the case of B^+ ion implantation, at the fivefold overlap [42]. The limiting defect concentration a cluster must have for silicon to become amorphous is approximately 5×10^{21} cm^{-3} [43].

Now what types of defects are responsible for the lattice period increase observed in silicon under high-energy particle irradiation? To obtain the answer it is necessary to consider the nature of lattice period recovery in implanted silicon subject to the annealing process.

The recovery of a Si^+ implanted silicon lattice for isochronal (15 min) annealing is given by curve *1* in Fig. 9. The lattice period recovers in two basic stages: at

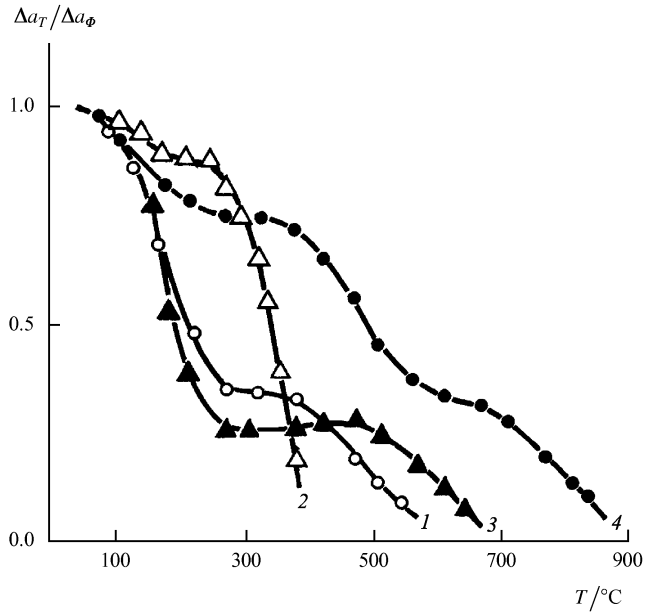

Figure 9. Lattice period recovery in silicon implanted with Si^+ (*1*), Li^+ (*2*), P^+ (*3*), B^+ (*4*) following isochronal annealing [47].

100–280 °C and 380–600 °C. For neutron irradiated silicon, the defect annealing is complete at 700 °C in the bulk and at 600 °C at the surface of the crystal [44]. The lower defect annealing temperatures seen in implanted layers and in the surfaces of neutron irradiated crystals are associated with the fact that the surface is a sink for radiation-produced defects.

The first stage of lattice period recovery coincides with the temperature interval of divacancy annealing. The second stage involves the annealing of polyvacancy complexes such as fivefold ones (Si–P1 centres) and some other complexes, not yet identified. As suggested by the data of Refs [45, 46], these complicated complexes do not form during the irradiation but rather during the subsequent treatment and are the product of the structural rearrangement of the defects.

To prove that the first stage is mainly the annealing of divacancies, a defect annealing experiment on Li^+ irradiated silicon was made [47]. Under Li^+ irradiation the divacancy production in silicon is as effective as for other light ions, but a divacancy annealing stage is in this case absent.

Upon thermal treatment at about 80 °C lithium becomes mobile and is trapped by divacancies. The resulting complexes are annealed out at higher temperatures than divacancies [48]. A similar situation occurs with lattice period recovery. In Li^+ implanted silicon the lattice period recovers in the same temperature interval as that where lithium divacancy complexes are annealed (curve *2* in Fig. 9). The importance of this experiment is in the proof that vacancy defects can increase the lattice period of silicon.

By analogy with metals, some authors [49, 50] assume that vacancy defects must reduce the lattice period in silicon and that its increase can only result from interstitial defects. In covalent crystals the situation is more complex than in metals. Broken bonds occurring near defects unite to form a 'defect' molecule. It is the nature of these bonds which determines whether the atoms in the first coordination sphere will relax into or out of the defect region. The lattice period decreases or increases respectively.

Calculations based on the EPR data [51] have shown that the sign of the atomic displacements in the region of a single vacancy in silicon depends on the charge state of the vacancy. For divacancies in the negative and positive charge states, the atomic displacements have the same direction, away from the defect, but the absolute magnitudes of the displacements are different for these two charge states. If the defect charge exchange is achieved optically or by charge carrier injection, the lattice must shrink and dilate at the frequency of the charge exchange of the prevailing defects.

Upon implanting impurity atoms, defect-impurity complexes appear in silicon. In silicon implanted with P^+ ions, in addition to E-centres [5], complicated complexes form whose annealing temperature is 100 °C higher than that of the intrinsic polyvacancy complexes (curve *3* in Fig. 9) [47].

In B^+ implanted silicon, defects that are annealed at the high-temperature 700–900 °C stage appear (curve *4* in Fig. 9). Their concentration is correlated with B^+ ion dose ($C_d \propto \Phi^2$) [52]. The formation of complicated complexes with radiation-produced defects involves Sb and As [41].

9. Stable complexes with interstitial silicon atoms

The concentration of EPR-identified room-temperature stable interstitial complexes is several orders of magnitude lower than that of divacancies [35].

Appreciable concentrations of interstitials are suggested by the data from internal friction studies of irradiated silicon [53]. Electron-microscopic investigations of residual damage in irradiated and subsequently annealed silicon have revealed the existence of implantation stacking defects [54]. These are presumably built up from the interstitial silicons that form during the break-up of interstitial complexes.

In Refs [47, 55] the x-ray diffraction method was used to determine the concentration and annealing temperature of stable interstitial complexes. The work relied on the well known phenomenon that Si interstitials push out Group III elements from the silicon lattice sites (Watkins effect). It was expected that the substitution process also takes place during the thermal treatment of the resulting samples provided the annealing of complexes liberates interstitial silicons.

The displacement of boron atoms from crystal sites is readily monitored by the change in the lattice period of the crystal. Boron atoms have a covalent radius of 0.8 Å, which is smaller than that of Si (1.175 Å), and so they shrink the silicon lattice when occupying its sites. As boron atoms are displaced from the sites, the lattice period is expected to increase. This is indeed the case in highly boron doped ($\rho_0 = 0.005\ \Omega$ cm) and implanted silicon. Superimposed on the lattice period recovery curves there are 'reverse annealing' stages (Fig. 10). In B^+ implanted silicon these are at 120 and 480 °C, and in the case of P^+ ions at 160 and 560 °C.

Defect annealing studies in silicon layers either implanted with Group III–V elements or excited by low-energy (10 keV) electrons have shown that annealing

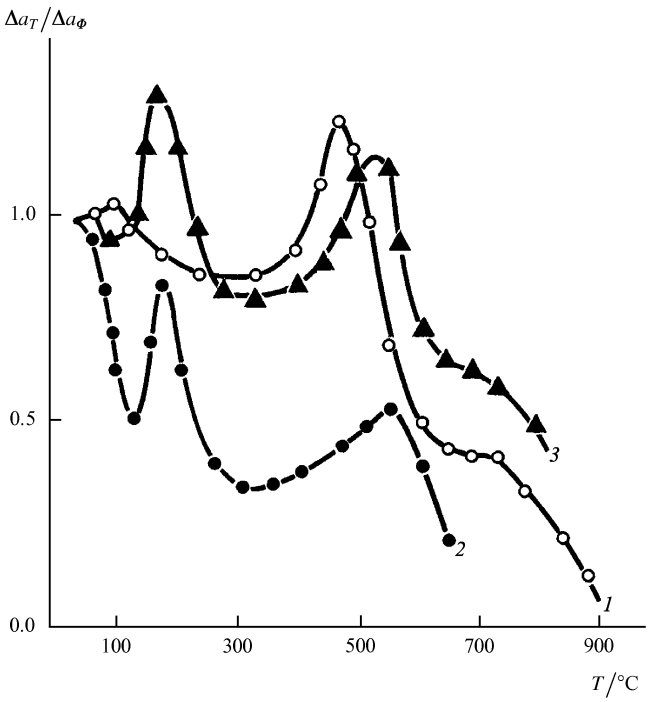

Figure 10. Lattice period recovery in highly boron doped silicon implanted with B^+ (*1*, *3*) and P^+ (*2*) [58].

temperatures for the interstitial complexes are charge state dependent [56]. In the positive charge state, the interstitial defects associated with Si–P6 and Si–B3 centres are annealed out at 120 and 480 °C respectively, whereas in the neutral charge state the temperatures are 160 and 560 °C [5].

In the positive charge state, thermal treatment causes Si–P6 centres to rearrange into a more stable Si–B3 configuration. This agrees with the EPR data [57]. In the neutral charge state Si–P6 centres are annealed (destroyed) by liberating mobile, interstitial Si atoms. Estimates show that the concentration of interstitial complexes is comparable with that of divacancies.

Now the question emerges: why is it that in highly B-doped silicon, boron atoms are not displaced already in the process of implantation? The site-knocked Si atoms are an order of magnitude more abundant than the stable complexes. Ref. [58] associates this with the charge state of the defects. During the implantation of ions into silicon a major part of the ion energy is lost in inelastic interactions (for 100 keV B^+ ions this is about 80%).

The high level of ionisation may lead to a situation in which primary radiation defects, including the knocked out silicons, will become charged by trapping nonequilibrium electrons. This will prevent them from substituting negatively charged boron atoms in lattice sites. This suggestion is substantiated by experiments on the thermal annealing of irradiated samples using an electron 'illumination' (curve *3* in Fig. 10) [58].

With the charge state of Si interstitials during implantation one can associate [58] the differences which, according to Refs [59, 60], exist in the fractions of boron atoms occupying lattice sites directly in the process. The reason is to be found in different implantation conditions, primarily in terms of ion current density. The fraction of site-occupying boron atoms is determined not only by vacancy trapping but also by the substitutional activity of Si interstitials, which depends on the ionisation state.

10. Agglomeration of radiation-produced defects in highly doped silicon

The work of Hirvonen and Eisen [61] has demonstrated that the dose of amorphisation of silicon does not depend on the level of boron doping up to concentrations of the order of 10^{20} cm^{-3}. In Refs [62, 63], the effect of Group III and V impurities on the silicon amorphisation dose was established at an impurity concentration of 4×10^{21} cm^{-3}. These experiments do not reflect the agglomeration of intrinsic defects, however. At this level of doping, the possible concentrations of complexes of radiation-produced defects with impurities are comparable to the limiting defect concentration corresponding to the transition of the material to the amorphous state.

Refs [41, 46] contain the data on the defect agglomeration process during Si ion implantation in n-type silicon layers doped to about 10^{19} cm^{-3} (see curves *2–4* in Fig. 8). At this level of doping n-type silicon exhibits higher rates of introduction and agglomeration of stable defects as compared to undoped samples. For doped layers one also observes that in the implantation layer the limiting defect concentrations corresponding to the onset of amorphisation are higher. Nevertheless undoped and highly doped n silicon have the same amorphisation doses. The amorphisation takes place at a triple overlap of the defect cluster.

The differences in defect formation efficiency are believed to be related to the intensities of the annihilation processes. In highly doped n-type silicon layers annihilation seems to be prevented by the barrier formed by mobile vacancies with like charges with Si interstitials on the one hand and stable defects on the other.

The regions where the defect annihilation is slowed down most effectively are those where they cluster. In this case there is no need for each stable defect to capture a charge carrier. The electrons trapped onto the outer shell of a cluster form a barrier which bars not only electrons (Gossick's model [65]) but also vacancies of like charge and Si interstitials from the region.

The suppression of the annihilation process gives rise to high defect concentrations in clusters and also increases the size of the defects. This explains the seemingly uninterpretable difference in the limiting values of Δa, the defect concentrations corresponding to the onset of amorphisation. The point is that defects are distributed nonuniformly in the clusters. The defect concentration has a maximum at the centre of a cluster and decreases toward its periphery.

Amorphisation sets in when the central regions of the clusters overlap. The defects on the periphery of the clusters do not participate early in amorphisation but do contribute to the observed change in the lattice period. This contribution is greater for highly doped silicon. The differences observed are not only in the efficiency of defect agglomeration but also in the defect production rate. It is necessary that the proposed model be adequate for the early irradiation stage as well. This is indeed the case as it is established that, in addition to the main displacement cascade, a number of subcascades form around it.

The mobile vacancies and interstitial silicons that disperse from the emerging cluster and subclusters pene-

trate these regions (created by one primary recoil atom) and may subsequently annihilate with stable defects. In highly doped silicon, because of the formation of a barrier, the level of annihilation is lower, implying a higher rate of production of stable defects.

The model discussed makes it possible to understand why it is that radiation-produced defects can agglomerate into amorphisation only if they are introduced in the form of clusters: an established fact which has not yet been explained [66]. Doping impurities are not the only source of defect charge interchange. Nonequilibrium charge carriers that emerge in the implantation process also participate in charge interchange.

In experiments on vacancy – divacancy afterformation under electron illumination it has been found that the nonequilibrium charge carriers preferentially trapped by vacancies are electrons [29, 30].

11. Effects due to interstitial silicon atoms

As mentioned, even after low-temperature implantation or after electron or neutron irradiation, isolated Si interstitials do not behave like electrically active centres in silicon. There are, however, secondary phenomena which are due to the appearance and migration of the interstitials and which are experimentally observable. Among these phenomena is, first of all, the displacement, from lattice sites, of silicon-substituting impurity atoms, in particular aluminium (acceptor). This phenomenon is often called the Watkins effect.

Apart from displacing impurity atoms from their sites, interstitial silicon atoms may also form complexes (for example, with boron and carbon atoms), the nature and symmetry of which has been elucidated by analysing the EPR spectra. If silicon crystals contain dislocations, these must act as natural sinks for interstitial atoms.

The process of displacement of Group III atoms by Si interstitials plays a major role in the electrical activation and diffusion of an implanted impurity in silicon. This process is believed to be associated with the 'reverse annealing' behaviour observed in the dependence of the charge carrier concentration upon the annealing temperature in B-implanted silicon [67], and with the anomalously high diffusivity of boron in ion-implanted silicon under pulsed annealing conditions [68].

The process of substitution leads to the redistribution of boron atoms into a 'fast' interstitial diffusion channel. The same explains the anomalous thermal diffusion of boron in surface-oxidised silicon [69]. The oxidation process produces excess Si interstitials. Watkins discovered that Group III elements are displaced from silicon lattice sites by Si interstitials formed in high-energy electron irradiated silicon at 4.2 K. This phenomenon was also seen at the lower temperatures of 1. 6 and 0.5 K [70, 71], which raised the question of the nonactivation (athermal) intrinsic migration mechanism in silicon.

According to Bourgoin and Corbett's model [72, 73], the migration of atoms through the lattice at such low temperatures is due to the fact that as an atom changes its charge state it makes a transition from one equilibrium interstitial state to another (from tetrahedral to hexagonal, etc.). A related model [74] introduces a relay-race mechanism of migration of a dumb-bell interstitial as its charge is changed. This mechanism assumes a random migration of Si atoms until they run into a Group III element in their way.

In Refs [75, 76] the displacement of substitutional impurities during the annealing of stable interstitial complexes was investigated as a function of the concentrations of both the complexes and impurities. Not only Group III but also Group V impurities were found to be displaced. The efficiency of displacement correlated with the amount of mismatch between the covalent radii of the impurity and silicon atoms.

A study was also made of how the process of substitution is affected by electron illumination and by doping by additional Group IV impurities. The authors of Refs [75, 76] concluded that the athermal motion of self-interstitials in the silicon lattice at very low temperature is a motion in the field of elastic strains produced by impurity atoms with covalent radii different from those of the matrix.

It proved possible to determine the radii of the spheres defined by the condition that when within such a sphere, interstitial silicons move directionally to impurity atoms. For B, Sb, P, and As, the radii of the displacement spheres are close to 200, 100, 40 and 0 Å. For Group IV impurities C, Sn, and Ge, they are approximately 250, 120, and 27 Å. The displacement of P atoms from silicon lattice sites directly under irradiation was observed using the EPR method in Ref. [77].

In the absence of substitutional impurities, interstitial Si atoms may agglomerate under low temperature irradiation. This conclusion is favoured by the data of Watkins [78] who observed the annealing of divacancies in low-temperature-irradiated silicon on warming to 140 K.

12. Conclusion

The application of ion implantation has enabled the advantages of planar technology to be employed in microelectronics. The use of high energy ions will permit the growth of multilayer structures, which must take integral microelectronics one step further.

In fast-neutron or ion irradiation, the prevailing type of vacancy defects in silicon, divacancies, are primary defects. Two types of interstitial complexes are also introduced whose concentrations are comparable to those of the divacancies. Their annealing temperatures depend on the charge state. When in the positive charge state they are annealed out near 120 and 460 °C; in neutral, near 160 and 560 °C. The agglomeration of radiation-produced defects until the amorphisation stage is entered is only possible if defect clusters are introduced.

The cause for the migration of interstitial silicon atoms in the silicon lattice at about 0 K are substitutional impurities. Interstitial Si atoms move in elastic strain fields created by atoms whose covalent radii differ from the host atom radius. The same mechanism appears to control the gettering properties of some heavy impurities not necessarily in a substitution position — rare earth elements, for example.

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