

## Ion Implantation Studies in Silicon

"Channeling" techniques have been applied to the study of ion implantation in silicon.

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The successful construction of transistors for electronic circuitry is based upon controlling the thermal diffusion of minute quantities of dopant elements (specific elemental impurities which affect the electrical resistivity of semiconductors) into semiconducting crystals, usually silicon. These dopant atoms occupy lattice sites in silicon and determine the electrical properties of the semiconductor. Elements in group V of the periodic table, such as phosphorus and arsenic, have one more outer electron than is required to fulfill the conditions for lattice bonding; these elements therefore donate their extra electron to the lattice (this is termed *n*-type conductivity). Elements in group III, such as boron and gallium, on the other hand, must accept one electron from the lattice in order to complete their bonding to nearby silicon atoms, thus producing an electron "hole" (*p*-type conductivity). The electrical characteristics of silicon devices are determined by the concentration and distribution in depth of these dopant species (donors or acceptors). In thermal diffusion, the maximum concentration is determined by the equilibrium solubility at the process temperature (900° to 1100°C); the

distribution in depth is determined by the diffusion constant and process time.

Ion implantation provides an alternative, although rather violent, method of introducing dopant atoms into the silicon lattice. A beam of dopant ions, accelerated through a potential of typically 10 to 100 kilovolts, is allowed to impinge on the surface of the semiconductor. The depths to which the ions penetrate and their distribution in depth depend primarily upon the incident energy and are typically between 100 and 10,000 angstroms. The total number of implanted ions is determined by the ion current and implantation time. An integrated flux of approximately  $10^{14}$  ions per square centimeter (much less than a monolayer) is a representative ion dose for forming *p-n* junction devices. The fact that the total number of implanted ions can be controlled independently of their distribution in depth (in contrast to diffusion processes) is an important aspect of the ion implantation technique. Furthermore, the number of implanted ions is controlled by the external system rather than by the physical properties of the substrate. For example, dopants can be implanted at temperatures at which normal diffusion is completely negligible and to concentrations far in excess of their equilibrium solubilities.

Although many devices with comparable or better performance than diffused structures have already been made, the use of ion implantation in

the technology of semiconductor devices thus far has not been very extensive. This results largely from the lack of a detailed knowledge of the stopping processes for heavy ions and of the properties which they impart to the implanted layer. As an implanted ion slows down and comes to rest, it makes many violent collisions with lattice atoms, thereby displacing them from their lattice sites (radiation damage). These displaced silicon atoms in turn displace others, the net result being the production of a highly disordered region around the path of the implanted ion. A heavy ion, implanted at room temperature with an energy of 40 kiloelectron volts, will, for example, permanently displace about 3000 silicon atoms. Thus the implanted ion creates a disordered region in which the crystal structure has been severely disrupted. The ultimate fate of the extra implanted ion is far from obvious under these conditions.

The overall objective of ion implantation is to produce a doped region whose electrical characteristics are determined solely by the dopant atoms located at well-defined positions in the semiconductor lattice. It has become clear that, unless implantations at room temperature are followed by annealing procedures, the disorder will dominate the electrical characteristics of the implanted layer. Furthermore, if during the implantation or subsequent thermal anneal, the implanted atoms migrate to precipitation centers instead of occupying regular lattice sites, their effect as dopant atoms will be lost. As a consequence, the two most important parameters which describe the nature of implanted layers are the annealing characteristics of the disorder introduced by the implantation and the location in the lattice of the implanted atoms.

There are many experimental techniques for the evaluation of implanted layers. Measurements of the Hall effect and sheet resistivity indicate the number of current carriers and their mobility. These measurements, however, do not distinguish unambiguously between electrical effects associated with lattice dis-

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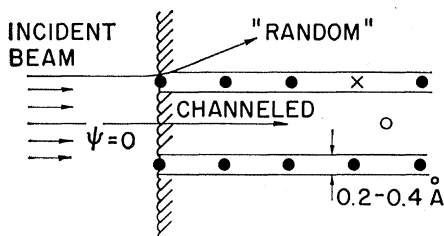


Fig. 1. Schematic diagram of a channeled beam passing through a crystal surface.

order and those of the dopant atoms. Transmission-electron microscopy can reveal the characteristics of the dislocations introduced during implantation and the subsequent anneal. The existence of such dislocations is not surprising, as there are large numbers of dislocations even in thermally diffused layers. Other techniques, such as electron and x-ray diffraction, can also be used to study lattice disorder.

In recent studies of ion implantation in silicon, the so-called "channeling" technique has been particularly valuable in the determination of both the number of displaced lattice atoms and the location in the lattice of the implanted dopant atoms. This technique is based on the fact that the interaction of a beam of 1-Mev protons or helium ions with a crystal lattice depends strongly on the orientation of the beam with respect to the crystal axes. Application of channeling techniques (described below) permits quantitative determination of the number of displaced substrate atoms and also of the number of dopant atoms on lattice sites. We here discuss our study of elements from group III (gallium, indium, and thallium) and group V (arsenic, antimony, and bismuth) implanted in silicon.

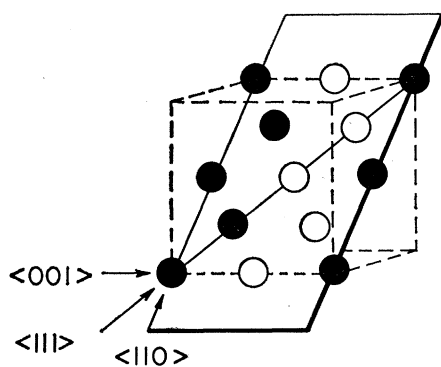


Fig. 2. Atomic configuration in the (011) plane of a diamond-type crystal: ●, lattice sites; ○, regular interstitial holes that are grouped in pairs along the  $\langle 111 \rangle$  atomic rows. Dotted lines indicate the outline of the unit cell.

## The Channeling Technique

In recent years, many different kinds of experiments (1) have established the fact that the motion of energetic atomic particles is strongly influenced by the regular arrangement of atoms that compose a crystal lattice. The general principles of the phenomenon (2) are quite simple, and indeed it might seem surprising that these effects did not become the subject of serious investigations until about 5 years ago.

Whenever an energetic charged particle (such as a 1-Mev proton or helium ion) moves through a crystal lattice making a small predictable angle with a close-packed atomic row (or plane), it will be steered through the lattice by correlated collisions with the lattice atoms. According to the theoretical treatment by Lindhard (2), such a steered (that is, channeled) particle will be deflected without penetrating closer to the center of the atomic row than approximately 0.2 angstrom (the Thomas-Fermi screening distance). Furthermore, the critical angle of approach for such a motion is given in the axial case by the formula:

$$\psi_{\text{crit}} = C \left[ \frac{(2Z_1 Z_2 e^2)}{Ed} \right]^{1/2} \quad (1)$$

where  $Z_1 e$  and  $Z_2 e$  are the nuclear charges of the moving particle and the lattice atoms, respectively,  $E$  is the energy of the projectile, and  $d$  is the atomic spacing along the chosen axis;  $C$  may be considered a proportionality constant which usually has a value close to unity. Typically,  $\psi_{\text{crit}}$  is of the order of a degree.

If the angle of approach to an atomic row is within the critical angle, then the particle is said to be channeled. On the other hand, if the angle of approach is larger than the critical angle, no correlated motion will occur; the particle will not "feel" the existence of a lattice structure, but instead it will move through the lattice as if it were composed of randomly distributed atoms. Of course, there are many directions of low index in a crystal, and it is sometimes difficult to specify an incident direction that does not lie within the critical angle of some plane or axial row.

If a beam of particles enters a perfect single crystal parallel to one of the major axes (Fig. 1), all of the beam cannot become channeled because some particles (as a result of their point of entry on the crystal surface) will under-

go a sufficiently violent collision with the first atom in an atomic row to be deflected immediately through an angle that is larger than the critical angle. This fraction of the beam cannot be channeled, and it is therefore referred to as the random fraction of the incident beam. If we define  $\psi$  as the angle between the incident beam and a particular low-index direction, we can specify two special conditions.

1) For the aligned case ( $\psi = 0$ ): The incident beam is equal to the channeled beam plus the random beam. Typically the channeled beam contains from 95 to 99 percent of the incident beam, depending on the particular lattice.

2) For the random case ( $\psi > \psi_{\text{crit}}$ ): The incident beam is equal to the random beam. In this case there are no channeled particles.

One aspect of the channeling phenomenon of particular importance is the fact that a channeled particle cannot approach closer to a lattice site than typically 0.1 to 0.2 angstrom (Fig. 1). Thus the crystal is divided into allowed and forbidden regions. This has some simple but rather important consequences. Those physical processes which require an impact closer than 0.1 to 0.2 angstrom [for example, wide-angle Rutherford scattering (3), nuclear reactions (4), or the production of characteristic x-rays (due to the interaction of the incident beam with the innermost electron shells) (5)] are not possible for a channeled particle. In consequence, a strong attenuation (up to 100-fold) is observed in the yield of such processes for the aligned case by comparison with the random case. The effect cannot go completely to zero since there are always some random particles (that is, 1 to 5 percent) even in the perfectly aligned case. These effects have been observed in numerous experiments and will be illustrated below. Large attenuations will occur not only for interactions with lattice atoms, but also with any impurity atoms located in the forbidden region for the channeled beam, for example, on lattice sites (x in Fig. 1). If, on the other hand, the atom being studied is located somewhere in the allowed region for the channeled beam (○ in Fig. 1), then no attenuation in the interaction yield will be observed, since now both the channeled and the random components of the beam can interact normally with the atom. Thus the channeling technique may be used to locate foreign atoms and also to determine the amount of lattice disorder.

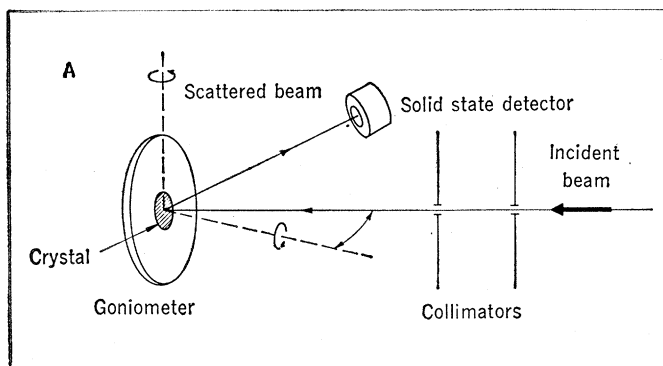
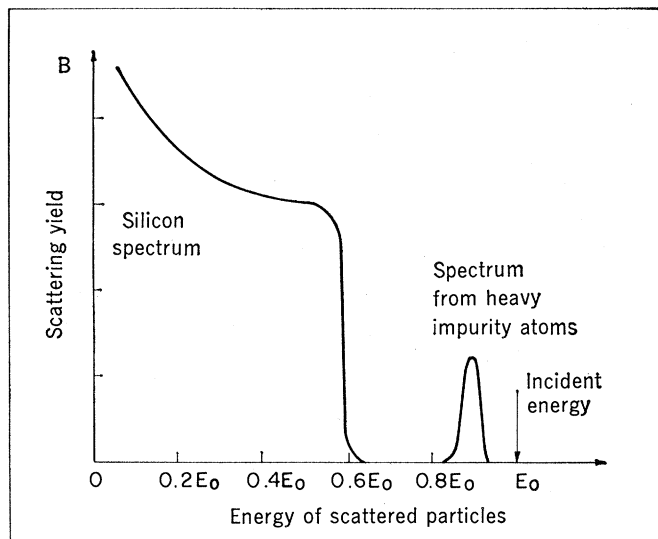


Fig. 3. (A) Schematic diagram of the experimental assembly used for the scattering experiments with 1-Mev helium ions. (B) Typical energy spectrum for the scattering yield of helium ions (incident energy  $E_0$ ) from an amorphous silicon target containing a heavy impurity (antimony) implanted within  $\sim 0.1$  micron of the crystal surface.



Let us now concentrate on the location of foreign atoms and see in detail how the technique works in a diamond-type lattice such as silicon. Figure 2 depicts the configuration of atoms in a (011) plane of silicon (all other positions within the unit cell have been omitted for clarity). This lattice consists not only of lattice sites (●) but also of unoccupied holes (○), which we will term the interstitial holes. Both positions are potential sites for an impurity atom. With a channeling experiment, along a  $\langle 111 \rangle$  [or a  $\langle 001 \rangle$ ] direction (Fig. 2), one is unable to distinguish between them, since the substitutional and interstitial sites both lie within the forbidden region for the channeled beam along these atomic rows. However, along a  $\langle 110 \rangle$  direction, the interstitial holes are not contained along the same rows as the lattice atoms; thus impurities in these holes will be exposed to the channeled beam. Consequently, by making measurements along a  $\langle 111 \rangle$  and a  $\langle 110 \rangle$  direction in silicon, one can determine what fraction of the foreign atoms are located (i) on lattice sites; (ii) in the regular interstitial holes along the  $\langle 111 \rangle$  direction; (iii) in some random location (for example, on a dislocation, at the surface, or in some other precipitation site).

One major difficulty has thus far been neglected: how to detect the foreign atoms at low enough concentrations so that the technique becomes useful. The interaction of the incident beam with the foreign atoms must give rise to a signal that can be cleanly distinguished from the much more numerous interactions with the lattice atoms. Fortunately, several methods are available. For implants of lighter atoms (such as

lithium or boron), we can often find a specific nuclear reaction that occurs with sufficiently high yield (6); in certain other cases, the yields of characteristic x-rays from the inner shells may be used. The most widely used technique (7-9) for analyzing the implanted layer is the measurement of the energy and orientation dependence of the yield of backscattered particles, that is, those particles that have been elastically scattered through an angle approaching  $180^\circ$ . This method is applicable to any system in which the implanted atoms are significantly heavier than those of the substrate. Let us now consider briefly how this technique works.

Figure 3A shows an experimental arrangement. The incident beam (typically 1-Mev helium ions), collimated to  $0.1^\circ$  or better, is allowed to strike a silicon crystal mounted on a suitable double-axis goniometer, which allows both a tilt motion and a rotation around an axis perpendicular to the base plate of the goniometer. Particles that have undergone wide-angle ( $\sim 150^\circ$ ) scattering are detected by means of a solid state detector, and their energy spectrum is recorded on a multichannel analyzer. Let us assume that the silicon target is amorphous (or a randomly oriented single crystal) with a small amount of heavier foreign atoms embedded near the surface. The resulting energy spectrum of the backscattered helium ions is shown in Fig. 3B. Particles scattered by silicon atoms at the surface lose a certain amount (41 percent) of their energy in the elastic collision with the silicon; thus the main part of the spectrum has a sharp threshold at  $0.59 E_0$  (where  $E_0$  is the energy of the incident beam). The prob-

ability of a backscattering event is extremely small; hence, most of the beam penetrates into the target, giving rise to a continuum of backscattered particles from greater depths in the crystal. These particles lose energy along their path in addition to the energy lost in the actual scattering event. They therefore emerge with lower energy, giving rise to an energy spectrum of scattered particles. This energy spectrum can be converted into a depth scale in which each interval of energy corresponds to a depth interval in the crystal from which particles are scattered. With a 1-Mev beam of helium ions, one can probe depths of up to  $\sim 1$  micron, with a depth resolution of  $\approx 300$  angstroms in the region near the surface. The shape of a typical energy spectrum is illustrated in Fig. 3B.

Scattering from an embedded atom that is heavier than the lattice atoms will cause a smaller loss of energy; thus these scattering events will be detected at higher energies, if the foreign atom is not embedded too deeply. In fact, for a shallow region of impurities (as in an implanted target), we will observe a well-separated impurity peak in the energy spectrum (Fig. 3B).

If the target is a single crystal, channeling effects will occur. These serve as a convenient way of orienting the crystal with respect to the incident beam (4); this is always the first step in the analysis of an implanted crystal. Once the desired orientations have been found, energy spectra are recorded along the  $\langle 111 \rangle$  and  $\langle 110 \rangle$  directions and also along a selected random direction. Figure 4, A and B, shows random and aligned spectra for a silicon crystal implanted at  $350^\circ\text{C}$  with 40-keV bismuth ions to a total dose of

$\sim 10^{14}$  ion  $\text{cm}^{-2}$ , and subsequently analyzed by a 1-Mev helium beam. Because of the channeling effect, the back-scattering yield in the silicon region of the spectra is reduced 30- to 35-fold when the crystal is aligned to a  $\langle 111 \rangle$  or a  $\langle 110 \rangle$  direction. Large attenuations are also observed in the scattering peak from the embedded bismuth atoms. Quantitative analysis shows that only 10 to 15 percent of the bismuth atoms can "see" the channeled beam along either a  $\langle 111 \rangle$  or a  $\langle 110 \rangle$  direction, which indicates that 85 to 90 percent of the bismuth atoms are located along both types of lattice rows. Hence, they must be located at the intersection of these two rows, namely, on the lattice sites (Fig. 2).

The aligned spectra for silicon (Fig. 4) reveal a small peak close to the maximum scattering energy, that is, close to the crystal surface. This is caused by disorder created during the implantation. The effect is more clearly illustrated by the dotted line, which shows an aligned spectrum for an implantation carried out at room temperature to a similar dose. In this case, the scattering yield from the region of the crystal affected by the implantation rises almost to random yield; this indicates that most of the silicon atoms in the doped region do not occupy regular lattice sites, and thus that severe damage

has occurred. Under these conditions [room temperature implantation of bismuth ( $\sim 10^{14}$  ion  $\text{cm}^{-2}$ )], there is also no attenuation in the bismuth portion of the scattering spectrum. This is not surprising, because most of the bismuth atoms are contained in the heavily disordered amorphous region and hence are not aligned with the underlying crystal rows.

In Fig. 4C, similar spectra are shown for a silicon crystal implanted at  $350^\circ\text{C}$  with 40-keV thallium ions to a dose of  $\sim 10^{14}$  ion  $\text{cm}^{-2}$ , and then subsequently annealed to  $650^\circ\text{C}$ . The silicon spectra are very similar to those in the bismuth implant. However, the scattering peaks from the foreign atoms behave quite differently. For thallium, no attenuation is observed along a  $\langle 110 \rangle$  direction, but about a 50 percent attenuation is observed along a  $\langle 111 \rangle$  direction. Thus 50 percent of the thallium atoms are located along the  $\langle 111 \rangle$  directions, but none of these are along the  $\langle 110 \rangle$  directions. We conclude from a study of Fig. 2 that 50 percent of the thallium atoms are located in the interstitial holes along the  $\langle 111 \rangle$  direction, and that no significant fraction occupies the substitutional sites. The remaining 50 percent are located elsewhere, that is, on dislocations, precipitation sites, or any other location that is displaced at least 0.2 angstrom from the lattice site.

## Lattice Disorder

Let us now consider in detail the behavior of dopants from groups III and V implanted in silicon. Before investigating the location of the implanted dopant atoms, we need to know how much lattice disorder has accompanied the implantation and how this disorder can be annealed (7).

As mentioned above, a peak in the aligned spectrum of silicon is an indication of lattice disorder. By measuring the area under this surface peak (Fig. 4A), we find that in hot implants (that is, those carried out above approximately  $300^\circ\text{C}$ ), less than 2 percent of the lattice atoms in the implanted region are permanently displaced even by an implantation dose of  $5 \times 10^{14}$  ion  $\text{cm}^{-2}$  (that is, several times the normal implantation dose). At room temperature, on the other hand, such a dose completely destroys the lattice structure in the implanted region, as shown by the fact that the dotted curve (Fig. 4A) rises to the random yield value. The dose dependence of this lattice disorder for implants at room temperature is illustrated in Fig. 5 (left side). For implantations of less than about  $5 \times 10^{13}$  ion  $\text{cm}^{-2}$ , the number of displaced lattice atoms increases linearly with dose; this is expected, since the individual damaged regions around the track of each ion are too far apart to interact with each other (typical radius of the heavily disordered region is 20 to 50 angstroms). At higher doses, these regions begin to overlap, and eventually an amorphous layer is formed. The slope of the linear portion of the curve (Fig. 5) indicates that each implanted 40-keV ion has produced  $\sim 3000$  displaced silicon atoms. Studies by electron microscopy (10, 11) on low-dose implants have shown that these individual disordered regions contain amorphous zones, presumably surrounded by defects of a more simple nature.

Figure 5 also illustrates the subsequent annealing behavior of the lattice disorder. At low doses, where individual disordered regions predominate, the main annealing stage occurs at about  $250^\circ\text{C}$ ; at higher doses, however, where an amorphous layer has been formed, much higher annealing temperatures are required ( $\sim 600^\circ\text{C}$ ). One simple way to minimize the lattice disorder is to maintain the lattice above  $300^\circ\text{C}$  throughout the implantation (Fig. 6). This hot implantation technique enables the individual disordered regions to anneal continuously during

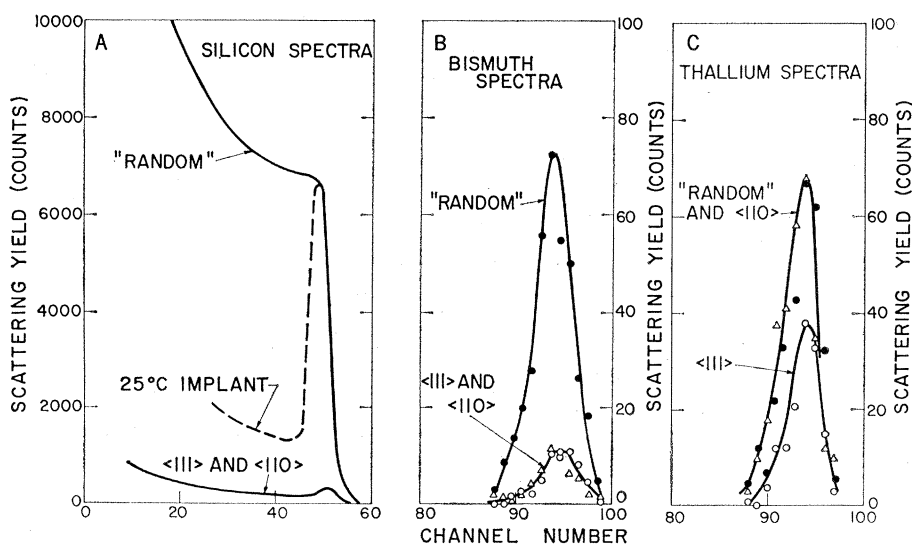


Fig. 4. Energy spectra (as recorded on a multichannel analyzer) for the scattering yield of helium ions from silicon crystals implanted at  $350^\circ\text{C}$  with: (i)  $\sim 10^{14}$  bismuth ions per square centimeter; (ii) with  $\sim 10^{14}$  thallium ions per square centimeter, followed by a 10-minute anneal at  $650^\circ\text{C}$ . The energy region corresponding to scattering from the silicon atoms is shown in (A), and that from the implanted bismuth or thallium atoms is shown in (B) and (C), respectively. In all cases, spectra are given for the incident beam parallel to a  $\langle 111 \rangle$  and a  $\langle 110 \rangle$  axis, as well as for a random direction. Dotted curve in (A) shows the aligned [ $\langle 111 \rangle$ ] spectrum for a similar bismuth implant at room temperature, which illustrates the much larger amount of lattice disorder accumulated under these conditions. The experimental points have been omitted from the silicon spectra for the sake of clarity.

the bombardment, thereby preventing them from overlapping to form the amorphous layer; this technique is now widely used in investigations of ion implantation.

Even though only 2 percent or less of the lattice atoms remain displaced after a hot implantation or in an annealed sample, this still represents  $\sim 10^{16}$  displaced silicon atoms per square centimeter in the implanted region. In other words, the number of defects still exceeds the number of implanted ions by a large factor. Consequently, interactions between implanted ions and residual lattice defects are quite possible.

One important generalization emerges from these studies of disorder: the dose and temperature dependence of the lattice disorder (Figs. 5 and 6) are not significantly affected by the atomic number of the implanted ion. The final location of the implanted ion in the lattice, on the other hand, is much more complicated and varies strongly from one element to another.

#### Lattice Location of Dopant Atoms

The lattice locations of ions implanted in silicon can be divided into three basic categories: (i) Substitutional dopants are those which exhibit a large attenuation in scattering yield along all major axes in the crystal. Dopants from group V (Fig. 4B) are the best examples of this group. (ii) Interstitial dopants exhibit a large attenuation along a  $\langle 111 \rangle$  or  $\langle 001 \rangle$  axis but not along a  $\langle 110 \rangle$  axis. Dopants from group III, under certain conditions (Fig. 4C), fall into this category. (iii) Nonregular dopants exhibit no significant attenuations along any crystal axis. Gold is a typical example. In this situation, the only conclusion one may draw is that the foreign atoms are not located on any regular site in the lattice and are therefore probably at some precipitation site, for example, at the surface, at a dislocation, or in a defect cluster.

Most implants do not fall cleanly into a single category. Thus, dopants from group III (gallium, indium, and thallium) usually involve both substitutional and interstitial components. Furthermore, even after annealing, there is always a measurable nonregular component, consisting of those implanted ions that have become trapped by the residual lattice disorder.

Let us now look at some of the differences in lattice-location behavior

between the implanted dopants from groups III and V. Significant differences have also been observed (6, 12) in their electrical behavior.

#### Implants from Group V (Arsenic, Antimony, and Bismuth)

Antimony is almost entirely in a substitutional position if it is implanted above  $\sim 300^\circ\text{C}$  (Fig. 6). Bismuth and arsenic exhibit similar behavior except that, in the case of arsenic, the substitutional content rises only to  $\sim 55$  percent. This difference between arsenic and the other dopants from group V illustrates how unimportant solubility arguments are in ion implantation. At these doses ( $\sim 10^{14}$  ion  $\text{cm}^{-2}$ ), the arsenic concentration is well below its solubility value at equilibrium, whereas antimony and bismuth exceed their equilibrium solubilities by about one and two orders of magnitude, respectively (13). Subsequent annealing treatment (Fig. 7) shows that no changes in the amount of substitutional component occur below  $\sim 900^\circ\text{C}$ ; this is also the temperature at which significant vacancy-type diffusion can take place. Even at  $900^\circ\text{C}$ , only bismuth shows a measurable falloff; presumably, this is associated with its much smaller solubility. Hence, even in a supersaturated system, it is possible to anneal the lattice disorder without causing excessive precipitation of the implanted dopant atoms. Implants made at room temperature follow a similar annealing pattern, except that the substitutional component of arsenic, antimony, or bismuth is generally not observed below  $500^\circ\text{C}$ ,

that is, not until the amorphous surface region starts to anneal.

Electrical measurements (12) for dopants from group V, implanted to a dose of  $10^{14}$  ion  $\text{cm}^{-2}$  or greater, show that a close correlation usually exists between the number of charge carriers (electrons) and the number of substitutional dopant atoms; both exhibit essentially the same implantation and annealing behavior. At lower doses, however, differences between electrical behavior and the number of atoms on lattice sites have been observed. This is attributed to the influence of the effects of irradiation damage similar to those found in silicon irradiated by fast neutrons (14).

In the case of phosphorus implants, the lattice location of the dopant atoms cannot be obtained by the scattering technique, because the mass of the phosphorus atoms is too close to that of the silicon atoms. However, electrical measurements (6) indicate for phosphorus an implant behavior similar to that of the heavier elements of group V.

#### Implants from Group III (Gallium, Indium, and Thallium)

Here the behavior is much more complex and depends strongly on implantation temperature and dose, as well as on subsequent annealing treatment. Furthermore, under identical conditions of implantation and annealing, considerable differences in behavior are observed between the individual elements of group III. Under certain conditions (Fig. 4C), a group-III atom may occupy the special interstitial holes characteristic of diamond-type lattices. Under

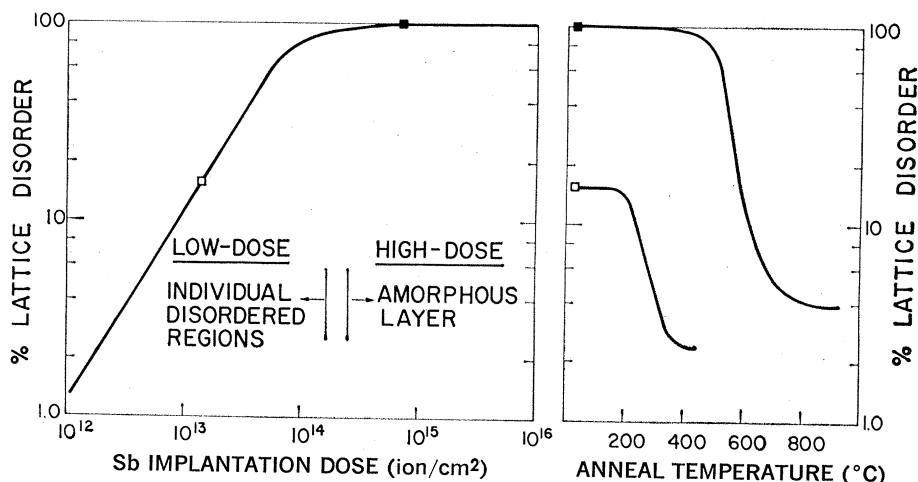


Fig. 5. Dose dependence and subsequent annealing behavior of the lattice disorder produced in silicon by implantation at room temperature with 40-keV heavy ions (gallium, arsenic, antimony, or bismuth). Experimental points have been omitted for the sake of clarity. Squares (■, □) identify the two anneal curves chosen (7).

other conditions, a pure substitutional component is observed, as was characteristic of elements of group V. The most common behavior, however, is intermediate between these two extremes, with the dopant from group III being almost equally divided between the substitutional and the interstitial sites.

Let us consider briefly the case of thallium implants (Fig. 8). After an implant at 450°C, the thallium atoms are distributed equally between substitutional and interstitial positions. However, on annealing, a rapid falloff in the substitutional component occurs at ~ 550°C, with a corresponding increase in the interstitial level. This indicates a movement of thallium atoms from lattice sites into the interstitial holes. Electrical measurements under identical conditions indicate a transition from *p*- to *n*-type behavior (that is, from acceptor to donor behavior) at about 525° to 575°C; this suggests that the interstitial thallium atoms are acting

as electron donors. At still higher temperatures, the interstitial component also falls off toward zero, an indication that the thallium atoms eventually migrate to some precipitation site (for example, to the surface or to a dislocation).

If, on the other hand, the implantation is carried out at room temperature—at a dose sufficiently low ( $\sim 10^{13}$  ion  $\text{cm}^{-2}$ ) so that the individual disordered regions do not overlap appreciably—then over 80 percent of the thallium atoms are found on lattice sites, and there is no detectable interstitial component. On annealing, these substitutional atoms all move to interstitial sites at about the same temperature as in the hot implant (Fig. 8) and then eventually to precipitation sites.

The same ratio of 1:1 between substitutional and interstitial components is also observed for hot gallium and indium implants, if the implantation temperature is kept below 450°C. Their subsequent annealing behavior, how-

ever, is quite different from that of thallium in that, as the annealing temperature is raised, the substitutional and interstitial components both decrease at roughly the same rate. This persistence of a 1:1 ratio between substitutional and interstitial components might suggest the existence of some sort of bonding or pairing process between substitutional and interstitial dopants. For the elements of group III such a pairing process may be aided by the fact that the substitutional (–) and interstitial (+) dopants have opposite charge states, whereas for the elements from group V the dopants probably have the same charge (+).

Another factor which contributes to the rather complicated behavior of elements from group III may be the replacement mechanism (15) which operates between a substitutional dopant and an interstitial silicon atom; namely: (substitutional dopant) plus (interstitial silicon) yields (interstitial dopant) plus (substitutional silicon). Interstitial silicon

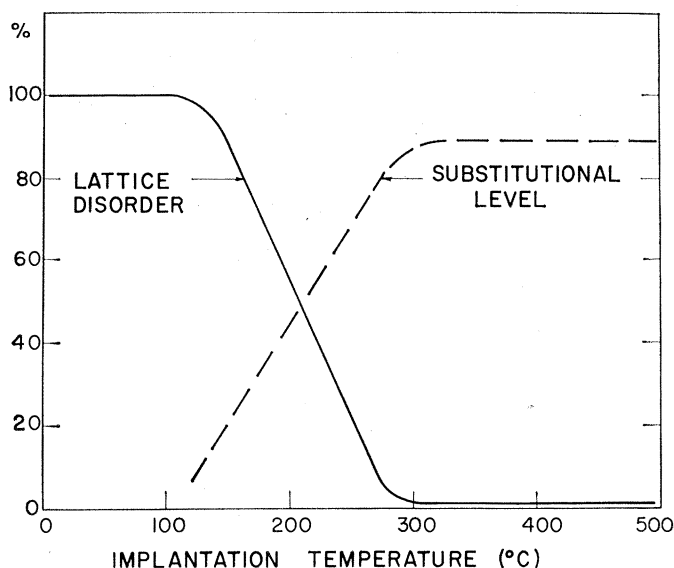


Fig. 6 (above left). Effect of implantation temperature on the lattice disorder and (dotted curve) on the substitutional content for antimony implants in silicon (9).

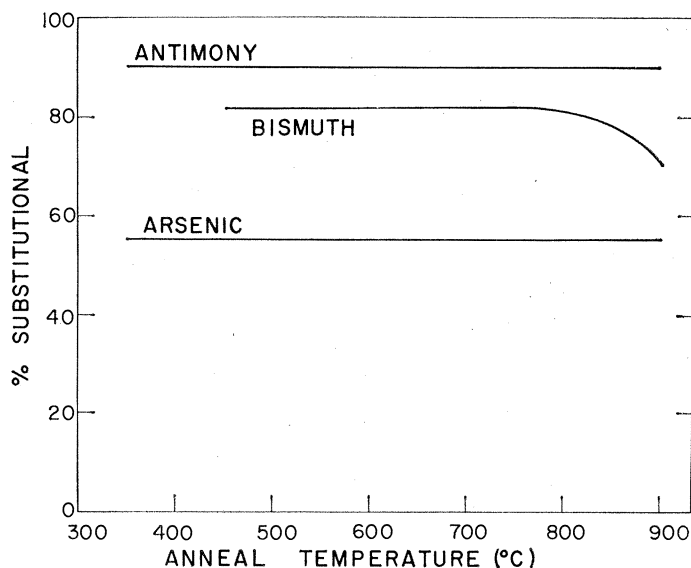
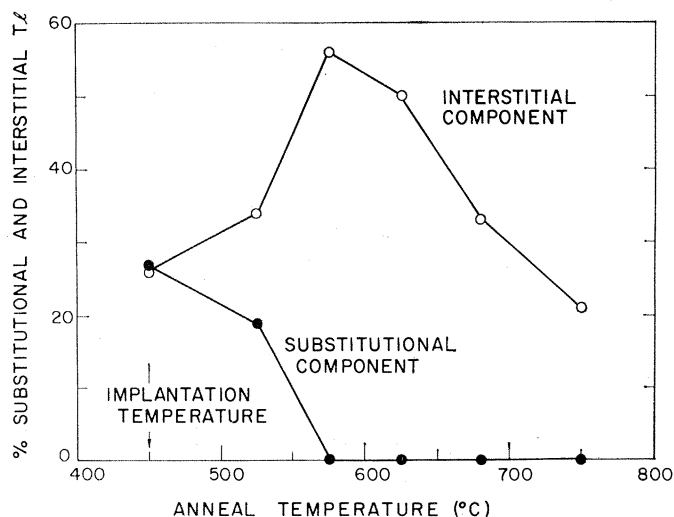


Fig. 7 (above right). Anneal behavior of various dopants from group V implanted in silicon at 350° to 450°C to a total dose of typically  $10^{14}$  ion  $\text{cm}^{-2}$  (9).

Fig. 8 (right). Anneal behavior of a thallium-implant at 450°C in silicon ( $\sim 10^{14}$  ion  $\text{cm}^{-2}$ ) (9).



atoms are produced in large numbers during the implantation and are known to be highly mobile at room temperature. Fairly convincing evidence for such a replacement mechanism has been obtained from studies by electron spin resonance techniques of silicon doped with aluminum (15) and also from some proton channeling studies of silicon doped with boron (8). Conversely, no evidence of such a replacement mechanism has been observed for any of the dopants from group V in silicon. Hence, this process might explain why only elements from group III exhibit the interstitial component.

### Summary

We have illustrated how the channeling technique can be used to locate foreign atoms and also to detect lattice disorder. This technique has the advantage of looking specifically and directly

at the implanted atoms. Its main disadvantage is the rather limited sensitivity. In the case of silicon, with a 1-Mev helium beam as probe, one may study a dose range of between  $10^{13}$  and  $10^{15}$  ion  $\text{cm}^{-2}$ . This is also the dose range of greatest present interest in ion implantation; thus this technique is useful for the analysis of implanted crystals.

We are still quite a long way from a complete understanding of the phenomenon of ion implantation. Clearly, the behavior of dopants from group III is much more complicated than that of elements from group V, and we do not yet have a detailed understanding of all the processes involved nor of their relative importance. However, the channeling technique permits one to obtain quantitative information on the location of the dopant atoms within the host lattice; this information may then be correlated with data obtained by electrical and optical studies, electron spin resonance, and other techniques.

## Immunoglobulin Structure: Variability and Homology

Amino acid sequences of immunoglobulins reflect evolutionary change and may explain antibody variability.

Frank W. Putnam

Immunoglobulins are proteins of animal origin, endowed with known antibody activity, and also include certain proteins related to antibodies in chemical structure and hence antigenic specificity (1). All these proteins are formed by the lymphoid cell system of vertebrates and circulate in the blood serum; they migrate electrophoretically as gamma globulins but are usually very heterogeneous, ranging into the beta globulins (2). Such heterogeneity precludes determination of structure by present methods of protein chemistry. In multiple myeloma, a tumor of the plasma cells which are normally a site of antibody biosynthesis, and in macroglobulinemia large amounts of homo-

geneous immunoglobulins are secreted into the serum, and incomplete immunoglobulins (Bence Jones proteins) may be excreted in the urine. These abnormal proteins almost invariably lack demonstrated antibody activity but are classified as immunoglobulins because of their similarity in site of synthesis, polypeptide chain structure, and antigenic specificity (3). The homogeneity of these abnormal proteins makes them more amenable to amino acid sequence analysis than normal  $\gamma$ -globulins and the natural mixture of antibodies. However, as a result of the success of sequence analysis of the abnormal immunoglobulins, considerable sequencing of normal globulins has been carried out.

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The abnormal proteins, though serving as a model for structural study of antibody  $\gamma$ -globulins, appear to differ in amino acid sequence for each patient, whereas the normal  $\gamma$ -globulins appear to have a mixed sequence as if they consisted of a mixture of proteins.

Because such almost infinite variability in primary structure is unique to the immunoglobulins it is thought to be related to antibody specificity. Though indirect, this is still the best evidence for the hypothesis that specific antibodies differ from each other in amino acid sequence. This is the crux of the antibody problem. How can an unforeseen agent (the antigen) impart recognition of itself into the somatic genome or express itself through the protein biosynthetic mechanism? This question leads to the paradox: Either protein structure is not invariant and is not uniquely determined by preexisting genes, or there must be already present in the genetic makeup of vertebrate animals enough immunoglobulin genes to provide for all the natural contingencies of life and the imagination of the organic chemist. To solve this problem knowledge is needed of the exact structure of immunoglobulins, and at present this is best obtainable by study of the abnormal globulins (3).

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