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THE EFFECT OF ION BOMBARDMENT ON THE PHYSICAL PROPERTIES OF SEMICONDUCTORS

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Features of the effect of bombardment by relatively slow ions (with energies up to 100 keV) on semiconducting materials are considered. Types of structure damage and methods and results of their investigation are described. Much attention is paid to the change of the electric properties of semiconductors following bombardment by ions, with an analysis of the advantages of ionic doping, a summary of the results of experiments on the electric conductivity of the irradiated layers and the changes occurring in it during the annealing process, and with data on the effect of ion bombardment on the behavior of the non-equilibrium carriers (radiative conductivity, luminescence). The change of the optical properties of semiconductors and the influence of bombardment on the diffusion of the impurities and on the chemical activity of the materials is also considered.

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I. INTRODUCTION

THE deceleration of an ion traveling through matter results from inelastic and elastic interactions. Processes are classified as inelastic collisions when the kinetic energy of the ion (or atom) is transferred directly to electrons of the target. The change in properties of semiconductors due to excitation of electrons (ion-electron emission, radiation-induced conductivity, and ionoluminescence) has been treated in[1], and I shall not take up this problem in this review. The elastic collisions, or as they are sometimes called, nuclear collisions, include processes of energy transfer from the moving particle to atoms of the medium that are not (directly) accompanied by excitation of electrons. Owing to elastic collisions, the energy of the ion is spent in forming defects (displacement of atoms from the sites of the crystal structure) and generating phonons. The change in physical properties of semiconductors under ion bombardment that involves introduction of various defects is the topic of this article.

I should make the reservation that the behavior of radiation defects created in semiconductors by fast electrons, neutrons, and light nuclei of energies ~1 MeV and higher has been rather well (and regularly) treated in a number of monographs and review articles (see, e.g.[2-5]). However, one can extrapolate the results reported in[2-5] only with great caution to the case of the radiation effect of ions of energies 1–100 keV, and not always even do that. First of all, this involves the fact that ions that penetrate only the surface layer of a semiconductor render it inhomogeneous through its thickness. Furthermore, although the ions create radiation defects that are apparently identical to those formed by fast-neutron irradiation, the final effect can still differ. This is because inclusion defects (the bombarding particles themselves) are simultaneously introduced during ion bombardment. The small depth of penetration of the ions gives rise to a change in the surface properties of the semiconductor, in particular, an appreciable change in the rate of recombination of carriers at the surface. The latter effect is not great when one uses strongly penetrating radiation. The limited range of the ions can have an appreciable effect on the subsequent fate (after their formation) of the radiation defects, since proximity to the surface can certainly affect their annealing. On the other hand, simultaneous introduction into a given region of the crystal of radiation defects and particles of the bombarding beam must also contribute to the course of annealing, provided that complexes between implanted atoms and radiation defects can be formed. I could continue to enumerate the features inherent in the action of ion bombardment on semiconductors, but I shall not do this now, lest I duplicate in the Introduction everything that I shall present in detail and systematically in the following sections of the article.

In studying the effect of ion bombardment on the physical properties of semiconductors, one must know the nature of the deceleration of particles in the material, the range, and the depth-distribution of the incorporated particles, the amount and spatial distribution of radiation defects, etc. Lindhard and his associates[6-8] have carried out a theoretical treatment of some of the stated problems for amorphous media. The methods of calculation of the number of defects that are primarily created by displaced atoms have been presented in detail in[2,3,5]. The effect of the crystal structure on the motion of ions has been

treated in the reviews[9,10] and in a number of theoretical papers (see, e.g.[11,12]). I shall barely discuss this set of problems in this article; the reader should turn to the specialized literature,[2,3,5-12] etc., if this is needed.

II. STUDY OF STRUCTURAL DAMAGE

1. Types of Defects

The simplest defects created in crystals by fast ions are Frenkel' defects, i.e., atoms of the target that have been expelled from their equilibrium positions and have been transferred to interstices, together with the empty sites (vacancies) thus created. The point defects also include particles of the primary beam that have been implanted into the semiconductor. In the general case, they can come to rest both at the atomic sites or in the interstices of the crystal structure. If we add to these defects antiisomorphous disorder (in a substance AB, A atoms occur in the B sublattice, or vice versa),[13] and take into account the possibility of formation of complexes involving radiation defects (see, e.g.[4]), the list of types of radiation damage still proves to be incomplete.

The point is that there is a range of velocities for most ions in which the fraction of the energy transferred to the atoms of the target can still appreciably exceed the threshold energy for displacement into an interstice, while the mean distance of free flight between collisions that produce defects becomes practically equal to the interatomic distance. This leads to formation of disordered regions in the crystal, which are usually called spikes or displacement peaks.[2] Thermal spikes can also arise directly in the process of deceleration of the ion. They are small volumes of the material that have been "heated to a high temperature" and then undergo abrupt cooling. We should also classify among the macroscopic radiation defects the depleted zones of a Seeger region, which contain vacancies in an amount considerably exceeding the equilibrium value.[14-16]

With electron microscopy, one can actually detect small disordered regions of several tens of Ångström units in diameter in semiconductors irradiated with ions.[17-19] As the dose is increased, i.e., the total number N of ions striking the target surface, the number of these regions increases. They can overlap when N is large enough, and give rise to a continuous disordered layer near the surface, which is apparently amorphous.[17,19]

On the other hand, we know of experiments whose results indicate that the reverse process can occur: crystallization of amorphous films. The authors of[20] have observed with the transmission electron microscope that xenon ions produced crystalline regions in amorphous films of germanium. Their linear dimensions grew with increasing energy (over the range 20–100 keV) from ~ 250 to 350 Å. In the opinion of the authors of[20], crystallization occurs in the displacement spikes as they interact with the simultaneously produced thermal spikes. They ascribe the lack of an effect upon bombardment with ions having $E < 20$ keV to the fact that the energy introduced into the micro-region of the target by the incident particle then proves to be less than the activation energy for the crystallization process.

As I have mentioned above, ion bombardment leads to multiple formation of Frenkel' point defects rather closely spaced together, or even to the formation of disordered regions. Hence, at temperatures that are not too low, such that the defects can migrate, they can coalesce to form dislocations. Formation of dislocations was observed in[17] upon annealing germanium that had been irradiated with O^- ions, and in[21], upon bombarding single crystals of silicon by 60-keV boron ions. As it turned out,[21] a dose $N = 3 \times 10^{16}$ cm^{-2} suffices to increase the dislocation density (they were revealed by chemical etching) from 5×10^3 to 3×10^5 cm^{-2}. In [19] they also detected appearance of dislocations upon crystallization of amorphous films of silicon owing to ions of neon, silicon, phosphorous, and boron of energies 10–90 keV.

A further specific feature of ion bombardment is that new phases can be formed at high enough doses.[19,22] In this regard, I should point out a possible way of synthesizing semiconductor compounds, as was carried out in[23] by bombarding tellurium films 0.1 μ thick with cadmium ions of energies 5–15 keV. The films obtained had hole conduction (excess tellurium), and the optical absorption spectra and photoconductivity were characteristic of CdTe. Irradiation of semiconductors by gas ions can also lead to formation of new phases: bubbles of gas into which the implanted particles collect.[24,25]

2. Methods and Results of Study of Structural Damage

Most often, people use electron microscopy and diffraction of fast or slow electrons to study radiation defects formed in solids upon ion irradiation.

Use of the electron microscope permits one not only to check the relief of a surface subjected to ion bombardment, but also to study (in working with thin films of a semiconductor) the formation and behavior of various defects whose dimensions attain several tens of Ångström units.[17-20,24-26,173-176] The very interesting results obtained in these experiments (apart from those mentioned above) amount to the following.

According to Parsons,[17] the dimensions of the disordered regions produced in germanium by 100-keV O^- ions proved to depend on the temperature of the specimen during irradiation (Fig. 1). According to

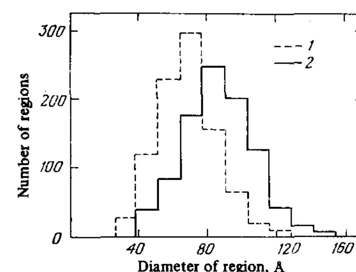


FIG. 1. Size distribution of disordered regions in germanium. Bombardment was performed at specimen temperatures of: 1–300°K; 2–30°K (from the data of [17]).

Parsons, the increase in the dimensions of these regions with decreasing temperature involves faster cooling in the thermal spikes. The latter are considered, along with the depleted Seeger zones, to be responsible for the formation of disordered regions.* If the bombardment is carried out at 320°C ($N \approx 1 \times 10^{15}$ ions/cm^2, current density $10^{10}-10^{12}$ ions/cm^{2}sec), then no disordered regions appear at all. Evidently, even if the stated regions are formed in this case, they rapidly crystallize epitaxially into the surrounding crystal. When the target is heated to $T > 320°C$, disordered regions that have been produced by low-temperature irradiation disappear. However, in regions of the target where its thickness is relatively great (a single-crystal substratum exists that hasn't been affected by ion bombardment), dislocation loops are formed. The number and dimensions of the latter gradually decline during annealing, owing to migration of vacancies. We can naturally ascribe the lack of dislocations in thin regions of the target to rapid diffusion of the excess vacancies existing in the disordered regions toward the two surfaces of the crystal (the irradiated side and the back), which are excellent sinks.

The authors of[173] have studied the structure of disordered regions in germanium with a transmission electron microscope.

According to the data of[19,174,175], annealing of silicon films that had been converted to an amorphous state by bombardment with Ne^+, P^+, Si^+, B^+, and Au^+ ions of energies 10–90 keV also led to formation of dislocations during the crystallization process. Here the dimensions of the dislocation loops increased over the temperature range 700–850°C. After specimens that had been irradiated with B^+ ions were heated for four hours at 800°C, precipitation of boron was observed. Appearance and growth of dislocation loops during high-temperature annealing has also been observed in films of gallium arsenide that had been damaged with neon ions.[176]

Use of fast-electron diffraction for massive single crystals (in reflection) showed that the surface layer of the target becomes less and less perfect with increasing dose when bombardment is performed at $T \lesssim 100°C$. Finally, it becomes completely amorphous at high enough doses.[28-34] Polycrystalline layers have been obtained in some cases.[29,33] The objects of study in these experiments were silicon,[28-30] germanium,[31,32] cadmium telluride,[33] and diamond.[34] Annealing of defects has been studied in[28,30] by the change in electron-diffraction patterns. According to[28], heating of a silicon specimen that had been preliminarily irradiated by helium ions at 850°C for an hour only partially anneals the defects. According to the data of[30], temperatures above 900°C are required for complete restoration of the structure of Si that has been damaged by phosphorous ions.

The method of taking electron-diffraction patterns in reflection in studying defects introduced by ion bombardment has the substantial defect that the electrons that give the diffraction pattern contain information on the state of only a very thin surface layer. As a rule, its thickness is considerably smaller than the depth of penetration of ions of energy ≈ 10 keV and greater. In line with this and for a number of other reasons, many investigators in recent years have turned to studying transmission electron-diffraction patterns, as obtained by passage of fast electrons through thin edges of massive single crystals prepared by etching,[17,19,177] or through unsupported films.[20,35,178] As the studies have shown, at high enough doses, the electron-diffraction patterns from regions that have been bombarded through by ions contain only diffuse rings corresponding to an amorphous state of the target material. When germanium was bombarded by 50-keV Ar^+ ions[35] and O^- with $E = 100$ keV[17], transition to the amorphous state was observed at doses $N \sim (1-5) \times 10^{14}$ ions/cm^2. About the same doses were required to render silicon amorphous upon irradiation by Ne^+, P^+, and Si^+ ions of energies 20–90 keV.[19] Gusev and his associates[177] have studied in detail the relation of the dose needed to render silicon amorphous to the nuclear charge of the bombarding particle. According to[177], as Z_1 varies from 3 to 83, the number of ions of initial energy 30 keV needed to convert the surface layer to the amorphous state declines at room temperature from 6×10^{16} to 2×10^{14} cm^{-2}. The problem of whether the transition to the amorphous state is due to overlap of disordered regions, or to accumulation of Frenkel' point defects, hasn't been finally elucidated yet (cf.[177,178]). Annealing of silicon that had been rendered amorphous by ion bombardment was studied in[19]. They showed that heating for one hour at 650°C leads to epitaxial recrystallization of the amorphous layer on the underlying layers of Si that hadn't been damaged by bombardment. The recrystallized layers were textured. Whenever the specimen was thin and was bombarded through (there was no single-crystal substrate), annealing gave a polycrystalline structure.

Low-energy electron diffraction has been used mainly to analyze the structure of the surface layer of semiconductors when alternating cycles of cathode sputtering and heating in a high vacuum had been used to obtain atomically-clean surfaces (see, e.g.[36-42]). According to these studies,* bombardment by relatively slow ions ($E \sim 100-500$ eV) renders the surface layer amorphous, but even brief annealing at $T = 400-550°C$ restores the diffraction pattern. It has been shown[38] that ion bombardment combined with annealing gives the same diffraction pattern as do cleavage surfaces after heating in a high vacuum. The fundamental results of the experiments using low-energy electron diffraction are reported in the review[42]. Hence, we shall take up further only the study by Jacobson and Wehner,[41] who conducted a detailed quantitative study of the formation and annealing of defects created in germanium by argon ions at room temperature. The authors of[41] found that the intensity I of any peak in the diffraction pattern after irradiation by a dose N is expressed in terms of the initial inten-

*I should point out that a recent paper [27] has proposed a different mechanism of formation of disordered regions.

*The objects of the studies were germanium, silicon, and $A_{III}B_V$ semiconductor compounds.

sity I_0 of the same peak by the formula

$$I = I_0 \exp(-2\bar{a}N), \tag{1}$$

where $\bar{a}$ is the mean damaged area in the surface layer per ion. Figure 2 shows the variation of I/I_0 obtained in[41], while Table I gives values of $\bar{a}$ for argon ions of different energies.

We see that the higher the energy of the bombarding ions is, the smaller the doses needed to damage the surface. Interestingly, when $E < 50$ eV, the values of $\bar{a}$ are smaller than the area per atom on the surface. That is, not all the incident ions in this case damage the structure. Heating for fifteen minutes at 300–400°C sufficed for almost complete restoration of the intensity I of the peaks. This process required a higher temperature for higher doses or energies of the ions. The argon implanted into the germanium was released at the same temperatures as the diffraction pattern was restored, but such a correlation is hardly unexpected.

It is technically a rather complicated problem to perform low-energy electron-diffraction experiments. On the other hand, as I've pointed out above, use of fast-electron diffraction to analyze radiation damage is also not always convenient and expedient. Furthermore, when one is working with a beam of fast electrons, the latter can alter the state of the object under study, as has been observed in[20,35]. Apparently, these changes are primarily due to heating of the target by the electron beam. However, it is not ruled out that defect formation* (e.g., according to the mechanism proposed in[43]) or annealing stimulated by the electron irradiation can contribute appreciably to the observed effect.

In this regard, the method described in[44] of studying radiation defects by using the angular dependence of secondary-electron emission is of interest. The idea of the method consists in applying the fact that the structure of the variation of the secondary-emission coefficient σ as a function of the angle of incidence of the primary electron beam is fully determined by the superficial layer of the single crystal. The merit of the method proposed in[44] consists in the possibility of varying the thickness of the layer being probed over a wide range by varying the energy of the electrons and the range of angles of incidence. Use of a pulsed method of measurement[46] with automatic recording of the curves makes it possible to reduce appreciably the dose of electrons required to get information on the structure of the objects being studied.

Table I

Energy E of the ions, eV	Mean area $\bar{a}$ of damage, cm²	Equivalent number of surface atoms
20	$7\cdot10^{-17}$	0.05
30	$7\cdot10^{-16}$	0.5
40	$1\cdot10^{-15}$	0.7
50	$1.4\cdot10^{-15}$	1
100	$2.6\cdot10^{-15}$	2
250	$8\cdot10^{-15}$	6
500	$4\cdot10^{-14}$	28
1000	$7\cdot10^{-14}$	50

Figure 3 shows the secondary-electron emission coefficient σ as a function of the angle of incidence of 2-keV electrons on the surface of a single crystal of germanium.[44] All the curves are shown on the same scale, but shifted with respect to one another along the axis of ordinates for convenience. We see from the graph that the structure of the $\sigma(\varphi)$ functions smooths out as the total number of potassium ions incident on the target surface increases (the bombardment was performed at room temperature in the ⟨110⟩ direction by 6-keV particles). When $N = 2 \times 10^{14}$ ions/cm², the angular dependence takes on a form characteristic of amorphous and polycrystalline targets. Heating the specimen at 650°K for 15 minutes restores the initial shape of the curve. This indicates complete annealing of the radiation defects. Analogous studies have recently been performed also on gallium arsenide bombarded with cadmium ions.[189]

We have applied this same method in our laboratory to study damage in germanium produced by hydrogen ions. At room temperature, it turned out that one must direct $(2-5) \times 10^{16}$ hydrogen ions of energies 0.5–5 keV at 1 cm² of surface of the crystal to attain a smooth angular dependence $\sigma(\varphi)$. Thus, the damaging action of hydrogen ions is about 100 times weaker than that of potassium ions. However, the defects formed in the

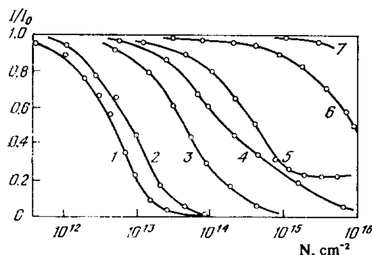


FIG. 2. Variation in intensity of diffraction peaks with increasing irradiation dose. The energies of the argon ions in eV are: 1–1000, 2–500; 3–250; 4–100; 5–50; 6–20; 7–10 (from the data of [41]).

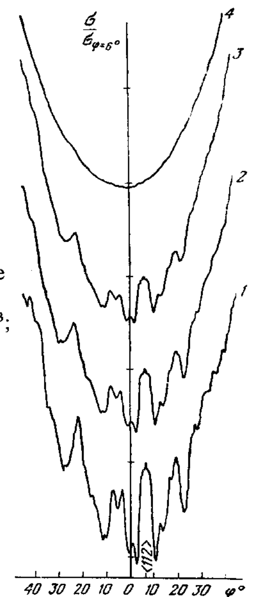


FIG. 3. Dependence of $\sigma/\sigma_{\varphi} = 6°$ on the angle of incidence of electrons. [44] Dose (ions/cm²): 1–0; 2–1.2 × 10^{13}; 3–4 × 10^{13}; 4–2 × 10^{14}.

*This is particularly true of crystals having ionic bonding (see [2,5,45]).

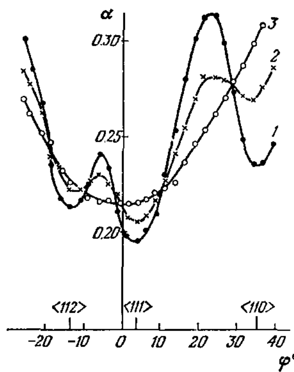


FIG. 4. Relation of the ion-electron emission coefficient of germanium to the angle of incidence of 10-keV ions. The density of the primary ion current j = 8 μA/cm². The target temperatures are: 1–611°K; 2–604°K; 3–593°K.

crystal upon hydrogen-ion bombardment proved to be considerably more stable,* for even heating for two hours at 800–850°C did not completely restore the initial shape of the $\sigma(\varphi)$ curves. Interestingly, one can also smooth out the $\sigma(\varphi)$ curve by bombarding germanium with hydrogen ions of energies below 180 eV, although radiation defects are apparently hardly produced by such slow ions. A peculiar feature of bombardment by low-energy particles is also manifested in the fact that heating in vacuo completely restores the $\sigma(\varphi)$ curve to its original shape.

In[47], the suggestion was made of using the non-monotonic character of the angular dependence of secondary emission upon ion bombardment that is inherent in single crystals in order to study the structure of the superficial layer of solids. As applied to radiation damage of crystals, the idea of this method consists in testing the type of angular dependence of the secondary-emission coefficient. It can be easily understood from Fig. 4. Damage to single crystals of Ge, Si, GaAs, and InSb by ions of neon, argon, krypton, and xenon has been studied by this method in[48-51,179,180]. It was found that the minimum target temperature T_C at which the angular dependences of the secondary-emission coefficients still do not differ from the curves obtained from a perfect single crystal is a function of the mass of the bombarding particles[48,49] and their current density.[50]

The authors of[50] have shown that when one applies a continuously-acting ion beam to a target in an established state, the logarithm of the density of the

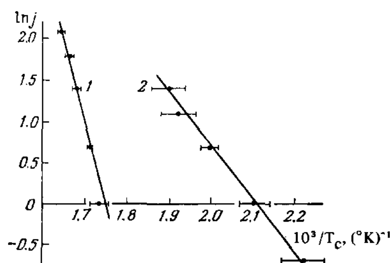


FIG. 5. Relation of the logarithm of the ion-current density j to the reciprocal of the temperature T_C. The value of j varied within the range 0.5–8 μA/cm². 1–xenon; [50] 2–hydrogen.

*We are considering the damage arising in the strongly damaged layers; for more details, see below.

primary ion current j must be a linear function of the reciprocal temperature T_C^{-1}. Here the slope of the $\ln j\,(1/T_C)$ line is determined by the energy of activation ΔE for elimination of the stablest defects introduced by ion bombardment. This is illustrated by the graphs drawn in Fig. 5. For germanium, the activation energies proved to be 1.8 ± 0.3 eV and 0.6 ± 0.2 eV for xenon and hydrogen ions, respectively. The considerable difference in activation energies shows that the properties of the stablest defects are determined by the type of bombarding particles, at least in one of the two cases. Experiments that I have performed jointly with Belyakov and Tsekhnovicher have shown that $(2-5)\times 10^{16}$ ions/cm² are required to render amorphous the surface layer of germanium and silicon when bombarded by hydrogen and helium ions of energies ~3 keV. Annealing of previously-damaged specimens for 2–3 hours at 800–850°C does not completely restore the structure. At the same time, annealing of crystals damaged by xenon ions is complete even at $T \leq 350$°C. I should note that if one performs the bombardment with helium or hydrogen ions at $T > T_C$, then an increase in the dose up to $\sim 1\times 10^{18}$ ions/cm², i.e., by two orders of magnitude, causes no appreciable change in the angular dependences. Hence it is clear that the "unannealed" disturbances are not defects that have been directly created by the ion during deceleration. Evidently, the stable defects only arise when the concentration of radiation defects or implanted atoms becomes large enough for formation of some type of complicated structural damage. For example, such defects might be complexes (association) involving the implanted ions, and vacancies, and atoms of the semiconductor knocked into interstices, or even coarser structures: dislocations or gas bubbles.

Cathode sputtering by ions is also sensitive to the structure of the superficial layers of the target.[52-57] For example, this might arise from the fact that conversion from the monocrystalline to the amorphous state alters the bonding of the surface atoms to the solid, and it also rules out the possibility of focused collisions. As was shown in[55], study of the temperature-dependence of the cathode-sputting coefficient at different ion-current densities permits one to determine the activation energy of annealing from graphs analogous to Fig. 5. According to[55], ΔE amounts to 1.15 ± 0.2 eV for germanium bombarded with argon ions of energy 100–800 eV. I must note that it is less convenient to study radiation damage to crystals and annealing of defects by using cathode sputtering than by ion-electron emission because of the greater complexity of the method.

A new method has been developed in recent years and successfully applied to study defects created by ion bombardment in germanium and silicon.[58-63,181-187] In particular, it permits one to determine the positions of the implanted atoms in the crystal structure. We can easily understand the idea of the method from Fig. 6, which shows the energy distribution of helium ions scattered by a single crystal of silicon at the angle 150°. The initial energies of the helium ions were identical, being 1 MeV. Hence, after Rutherford scattering at the given angle, the energy of a particle should depend on the type of nucleus of the target on

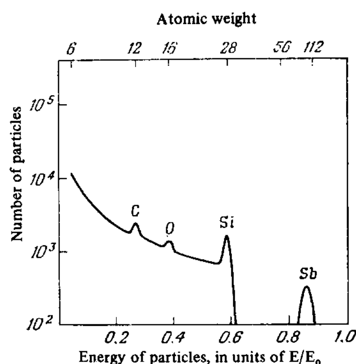


FIG. 6. Spectrum of helium ions scattered by a single crystal of silicon. [58] The initial energy E_0 of the He^+ ions is 1 MeV.

which it has undergone single scattering. Peaks are seen in the energy spectrum in Fig. 6 that correspond to scattering by nuclei of antimony, silicon, oxygen, and carbon concentrated in a thin surface layer of the single crystal of Si (the C and O nuclei are among the surface impurities, while the Sb nuclei were introduced into the Si by ion bombardment). The continuous spectrum extending to the left from the Si peak is produced by helium ions that have undergone multiple or single scattering within the interior of the crystal, and have lost an appreciable fraction of their energy in inelastic collisions. It is easy to understand that the area under any peak is directly proportional to the number of scattering nuclei of the appropriate type that can be "seen" by the helium ions. For simplicity, let us consider a square net made of atoms of type A (Fig. 7a). Then, under bombardment in the ⟨10⟩ direction, scattering can occur only from the A atoms of the left-hand row. However, if a fraction of the A atoms leave the lattice sites (Fig. 7b), then the number of scattering centers increases, and the area of the peak in the energy spectrum of the reflected particles increases proportionally. (Under the conditions of the experiments,[58-63,181-187] it suffices to shift an atom by ~0.2 Å from the axis of the atomic chain in order to bring it out of the shadow cast by the preceding atoms of the crystal. However, if atoms of type B have been introduced into the crystal as an impurity, then one can determine their positions in the crystal structure by comparing the energy spectra upon irradiation in different directions. In particular, in the case shown in Fig. 7c, the peak from the atoms of type B will differ from zero when one bombards in the ⟨10⟩ direction, but it will vanish upon irradiation in the ⟨11⟩ direction.

The fundamental results obtained in[58-63,181-187] upon bombarding germanium and silicon by Ga, As, Sb, In, Tl, P, Bi, Pb, and Xe ions of energies ~40 keV amount to the following. At room temperature, each heavy ion displaces several thousand atoms from their sites in the structure.* Consequently, isolated disordered

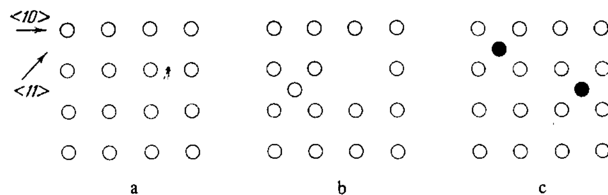


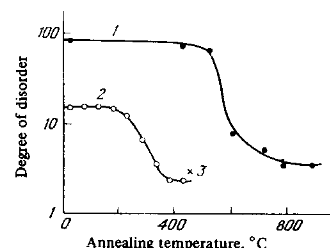
FIG. 7. Models of a plane square net made of atoms of type A (○) a) net without defects; b) net containing Frenkel' defects; c) net containing impurity atoms of type B (●) in the interstices.

regions are created near the trajectories of the individual particles. According to[181], the number of defects created in silicon by bismuth ions increases linearly with increasing energy over the range 20–225 keV. At doses $N \leq 10^{13}$ ions/cm², at which these disordered regions do not yet overlap, annealing at 180°C is required to restore the structure for Ge, and 260°C for Si. Increase in the dose leads to overlap of the previously isolated regions, and to an increase in the temperature required for restoring the structure. At doses $N \sim 10^{15}$ ions/cm², at which the surface layer becomes amorphous, these temperatures now are as much as 380° and 570°C for germanium and silicon, respectively. Figure 8 shows the results of constant-time (t = 10 min) annealing of silicon. We see from the diagram that one should perform the ion doping at elevated temperatures, rather than room temperature, in order to diminish the radiation damage to the semiconductor.

The authors of[182-184] have also observed for silicon that the rate of accumulation of radiation defects decreases with increase in the temperature at which the implantation is performed. Moreover, they note in[184] that the degree of disorder at constant dose depends appreciably on the density of the ion current. Thus, for example, in bombarding with boron ions, a decrease in the current density from 2 to 0.2 μA/cm² led to a decrease in the degree of disorder by a factor of three (implantation was performed at room temperature; $N = 1 \times 10^{16}$ cm^{-2}). The rate of damage to the crystal also proved to be a function of the direction of bombardment: it is about twice as small in irradiation along the ⟨110⟩ axis as for a random direction.

Localization of the implanted atoms in the structure depends on many parameters: the type of ions, the dose, the temperature at which implantation is performed, and the temperature of annealing. According to[185,186], when implantation is performed at room temperature, about 80% of bismuth and thallium ions come to rest at substitutional sites when the dose does not exceed 10^{13} cm^{-2}. For larger doses $N \geq 10^{14}$ cm^{-2}, additional heating is needed to transfer the implanted

FIG. 8. Variation upon annealing of the degree of disorder produced in the structure of silicon by Sb^+ ions. 1, 2–doping at 25°C; 3–doping at 450°C. The doses (ions/cm²) were: 1-4.5 × 10^{14}; 2–1.1 × 10^{13}; 3–3 × 10^{14}. [58]



*We recall that in these experiments an atom deviating from its equilibrium position by more than 0.2Å was already detected as a displaced atom. However, since introduction of a single defect (e.g., a vacancy) should distort the structure in its vicinity, the number of defects detected in [58,61] should appreciably exceed the number of atoms that have been displaced from their sites directly by the moving particles.

particles to substitutional sites if implantation had been performed at $T \approx 20°C$. Here the sites become occupied simultaneously with annealing of the radiation damage. One can also attain the maximum possible occupation of substitutional sites by implanted atoms by bombarding the crystal at 350–450°C.

Atoms of the third and fifth groups of the periodic table behave in different ways. The fraction of pentavalent atoms (As, Sb, Bi) occupying substitutional sites is as much as 75–90%, and it does not depend on the dose over the range $10^{13} \leq N \leq 10^{15}$ cm^{-2}, provided that the crystal structure is preserved during implantation. On the other hand, according to the data of[62,186,187], when silicon heated to 350–450°C is irradiated with ions of trivalent elements (Ga, In, Tl), the implanted atoms are distributed with approximately equal probability in substitutional sites and in normal interstices lying along the ⟨111⟩ rows. During annealing at $T > 450°C$, the number of trivalent atoms in substitutional sites declines, while that in the interstices rises correspondingly. Here the interstitial Group III atoms are apparently donors in Si, rather than acceptors (see, e.g.[193]).

The more complex behavior of Group III atoms has been ascribed,[189] in particular, to the possibility of exchanging places between a substituent atom and an atom of the main substance occurring in an interstice. Interestingly, the number of trivalent atoms occupying substitutional sites can be varied by introducing pentavalent atoms into the crystal (the order of bombarding has no significance).[187] Thus, for example, when silicon is irradiated with arsenic and thallium ions, 50% of the Tl atoms occupy substitutional sites when $N_{As} = N_{Tl}$. When $N_{As} = 6\,N_{Tl}$, 75% of the trivalent atoms now occupy substitutional sites.

Table II gives information on localization in Ge and Si of atoms implanted by ion bombardment, as taken from[63]. We see that all the impurities but indium behave in about the same way in germanium and silicon. From 80% to 90% of all implanted atoms of Sb, Bi, Sn, and Pb can be transferred to substitutional sites. The numbers of Tl atoms occupying substitutional sites and normal interstices on the intersection of the ⟨111⟩ and ⟨110⟩ rows are approximately equal. This is also characteristic of In atoms in Si. However, 75% of all the indium atoms can become concentrated in substitutional sites in germanium.

Unfortunately, the method of study described above has the defect that large doses of probe ions ($\sim 6 \times 10^{15}$ ions cm^2) are required to make reliable measurements. (We recall that only 10^{16} particles per cm^2 are required, according to our data, for 3-keV helium atoms to render the surface layer amorphous.) Apparently, the observed lack of variation in the energy spectra of the scattered particles in the course of the experiment in[58] is explained only by the fact that the radiation damage is concentrated at the end of the range (i.e., far from the surface of the crystal) when one uses fast ions of energy 1 MeV.

Table II

Type of impurity	Percent of impurity atoms situated along the given row				Type of impurity	Percent of impurity atoms situated along the given row			
	Ge, ⟨111⟩	Ge, ⟨110⟩	Si ⟨111⟩	Si ⟨110⟩		Ge, ⟨111⟩	Ge, ⟨110⟩	Si, ⟨111⟩	Si, ⟨110⟩
Sb	90	85	89	87	Tl	65	35	84	46
Bi	76	80	87	86	Sn			92	96
In	75	75	52	25	Pb	87	85		

If the impurity atoms are radioactive, then their localization in the crystal structure can be determined by studying the angular distribution of a particles, electrons, or positrons emerging from the crystal. Here one uses the fact that the shadow effect has the result (see, e.g.[64]) that minima of yield will be observed in the directions of the atomic chains for light positive particles emitted from substitutional sites. The pattern is the opposite for electrons. In particular, this method has been used by the authors of[65] to determine the localization of atoms of ytterbium introduced into a single crystal of Si by ion bombardment. They found a minimum of yield of β particles in the ⟨110⟩ direction, and a peak in the ⟨111⟩ direction. This indicates that the Yb^{175} atoms lie in the ⟨111⟩ row, but outside the ⟨110⟩ row.

The shadow effect has also been used for research using the so-called proton-blocking patterns of amorphization and annealing of semiconductors (see, e.g.[66]).

I should note that the sensitivity of the described methods for detection of defects can be considerably enhanced by directing a probing beam at the specimen, and detecting the scattered particles along low-index directions.[190,60,191] Then the conditions for channeling are satisfied for the primary ions, and those for shadowing for particles scattered at a large angle by the atoms of the crystal structure. Consequently, the contribution to the detector signal from ions scattered by the ordered part of the crystal is considerably suppressed.

X-ray diffraction can also be used to study defects created by ion bombardment. An example of such experiments is[192]. In particular, its authors have established that elastic strains of the crystal extend into the interior to a depth of ~180 μ when diamond is bombarded by 40-keV lithium ions, although the thickness of the damaged layer is about 0.6 μ.

III. CHANGE IN THE ELECTRICAL PROPERTIES OF SEMICONDUCTORS UPON ION BOMBARDMENT

The main result of irradiating semiconductors with ions is to introduce various types of defects into the superficial layer of the target. The thickness of this layer is determined by the depth of penetration of the bombarding particles. In the general case, these defects can serve both as sources of mobile charge carriers (donors or acceptors), and as centers for scattering, recombination, and capture of carriers. Hence, bombardment alters not only the electrical conductivity of the surface layer, but also a number of other of the electrophysical properties of the semiconductor. In a number of cases, the action of the defects can extend far beyond the layer treated by the ions. For example, this occurs in the phenomenon of radiation-induced conduction, in which the diffusion distance of the current carriers in the semiconductor appreciably exceeds the depth of penetration of the ions.

1. Creation of p-n Junctions by Ion Bombardment

Studies on interaction of ions with semiconductors have been stimulated to a considerable extent, on the one hand, by the need of increasing the radiation stability of semiconductor devices, and on the other hand, by hopes (already partially justified) of using ion doping to create semiconductor devices that are more refined than those obtained by the method of diffusion or fusing-on. We shall take up below the advantages that ion doping has, as compared with other methods of preparing p-n junctions.

The ion-doping method is convenient primarily because using a beam of charged particles makes it possible to control the process of preparing semiconductor devices by using electric and magnetic fields. Indeed, one can shift the beam over the surface of the target, and vary its transverse dimensions and shape. By controlling the size of the ion current and the time of bombardment, one can introduce into the semiconductor strictly-defined amounts of the doping impurity. Here the use of mass separators makes possible high chemical purity in the technological process. Here we must bear in mind the fact that the surface being irradiated must be free from macroscopic "impenetratable" contamination.[67] Otherwise, regions shunting the junction will appear after the contacts have been applied. It is also desirable that the surface should not contain an adsorbed coating or other contamination because their atoms will be knocked by the primary particles into the interior of the semiconductor. Thus the electrophysical properties of the superficial layer can be altered (Fig. 9). However, sometimes one deliberately creates a foreign-type film on the surface of a semiconductor, e.g., a protective SiO_2 film through which ion doping is performed.[21 69-71] The distribution of particles implanted into a semiconductor by ion bombardment (see, e.g., the review [10]) differs from the impurity distribution introduced by diffusion or fusing-on. Here, by varying the energy of the bombarding particles and the orientation of the beam with respect to the crystal axes of the monocrystalline target, one can control not only the depth of penetration, but also the profile of distribution of the impurity. Simultaneously, the total number[2,72,73] and distribution in depth of the radiation defects will vary.

Another merit of ion doping is that one can introduce impurities into a semiconductor that could not be introduced in another way for some reason (low diffusion coefficients, low solubility, etc.) Thus, for example, the authors of[74] were not able to convert p-type to Si n-type by diffusion, nor by fusing-on of sodium. Nevertheless, bombardment by sodium ions formed an n-type layer on the surface. Here they could attain a concentration of active centers (donors) of $\sim 10^{20}$ cm^{-3}. Interestingly, according to[74], sodium atoms implanted in silicon by ion bombardment penetrate in one hour at 600°C to the same depth to which they can be introduced by diffusion from the melt (T = 800°C) in one week! The authors of[74] explain such substantial differences in the diffusion coefficient and in the electrical activity of the atoms implanted in different ways as follows. In ion bombardment, a considerable fraction of the atoms come to rest in the interstices upon being decelerated (in this regard, see[75]). In such a position, a sodium atom gives rise to a shallow donor level, and the diffusion coefficient over the interstices is relatively large. However, if one tries to introduce sodium by thermal diffusion or fusing-on, then in this case (under conditions close to equilibrium), these atoms will migrate via vacancies (with a low rate of diffusion). Furthermore, a sodium atom occupying a substitutional site is electrically inactive in silicon.

According to[76], the behavior of nitrogen in silicon and germanium also depends on the method of doping. In diffusion, nitrogen penetrates into the crystal in the form of N_2 molecules that have rather small dimensions and high energy of dissociation. The molecules do not give rise to electrically-active centers. Upon ion bombardment, nitrogen is introduced in the atomic state. In the opinion of the authors of[76], donor centers are formed by transfer of the nitrogen atoms to substitutional sites. The junctions obtained in[76] by bombarding p-type Si with nitrogen ions of energy ~ 60 keV had a rectification coefficient of $\sim 10^5$ at 1 V after annealing ($T \geq 700°C$).

With regard to impurities that can be relatively easily introduced into a semiconductor by ordinary methods, here also ion doping has the substantial advantage that it permits one to gain concentrations considerably exceeding the solubility limit under equilibrium conditions. This was noted as early as 1957 by Lander,[77] who was able to attain by ion bombardment a concentration of hydrogen in ZnO 10^5 times greater than the equilibrium value (hydrogen is a donor impurity with an activation energy of 0.05 eV). McCaldin and Widmer[78] were able to get the same degree of supersaturation of silicon with cesium in creating layers having n-type conduction by bombarding p-type Si with Cs^+ ions having E = 10 keV. It is especially to be noted that precipitation of cesium was not observed in this case, even at relatively high temperatures, owing to smallness of the diffusion coefficient.*

A plus feature of ion doping is the fact that lower temperatures are needed, as a rule, for annealing of radiation defects and transport of the implanted atoms to active positions (if such is required) than those at which diffusion or fusing-on take place. This rules out the irreversible processes that occur in semiconductors at high temperatures: diffusion and formation of

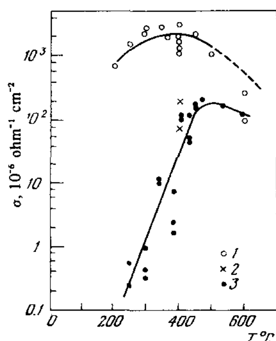


FIG. 9. Relation of the conductivity of the doped layer to the temperature of the single crystal of silicon during bombardment. E = 8 keV, (110) face, j = 0.3 $\mu A/cm^2$ for Na^+, j = 3 $\mu A/cm^2$ for Cs^+. 1—p $\approx 10^{-9}$ Torr, with preliminary heating of the target; Na^+; 2—p $\approx 10^{-5}$ Torr, Na^+; 3—p $\approx 10^{-5}$ Torr, Cs^+. [68]

*For more details on studies along this line, see the review. [68]

recombination centers. This simplifies the possibility of designing integrated circuits,[69,79] and thus one can diminish bulk recombination,[68,80,81] as is essential, e.g., in converters of light energy into electrical energy (the so-called solar cells).

The first studies on the action of ion bombardment on semiconductors[82-86,28,29] were conducted in connection with attempts to improve the electrical characteristics of metal-semiconductor point contacts. Although it was possible in a number of cases to get a positive practical result, these studies gave no unambiguous answer to the problem of the relation of the effect to the type of ions. Only in 1961 did Bredov and his associates[87] treat the influence of radiation defects and implantation defects on the electrical properties of a semiconductor. They showed that the action of the latter can predominate under certain conditions. Shortly thereafter, reports appeared on the first p-n junctions created in silicon by bombardment by Group III and V ions[88] and by lithium ions.[89]

Annealing of radiation defects during or after ion bombardment rather quickly made it possible to master the construction of semiconductor devices that were not only not inferior, but often even surpassed in their parameters the best specimens obtained by the diffusion method.[90-93,69,80]

Recently, p-n junctions have been created by ion implantation in germanium, silicon, gallium arsenide,[94,95] cadmium selenide and sulfide,[71,96-98,194] zinc telluride,[195] etc. We should note especially studies on doping of diamonds.[34,68,69,91,99,196-199] In[34] layers having n-type conduction were obtained by bombarding p-type semiconductor diamonds with hydrogen and nitrogen ions, and in[69] with phosphorus, and in[68] with alkali-metal ions. Vavilov and his associates[99,197-199] have studied doping of diamonds by lithium, boron, carbon, aluminum, and phosphorous ions. They found that one can vary the electrical conductivity of the surface layer by 5—10 orders of magnitude by varying the dose. Bombardment by Li^+, C^+, and P^+ ions produced donor centers, while irradiation with B^+ and Al^+ ions gave acceptor centers. The activation energy for electrical conduction lay in the range 0.2—0.45 eV.

Several interesting studies have also recently been conducted on doping of gallium arsenide crystals by various ions.[200-204]

2. Electrical Conductivity of Layers Obtained by the Ion-doping Method

a) Alkali-metal ions. McCaldin and his associates [68,74,78,79,91,100] and Medved and his associates [101,102] have studied the change in electrical conductivity of p-type Si upon bombardment by alkali-metal ions. (Some of the results obtained in these studies have already been discussed above). It was found that bombardment of p-type Si by even relatively slow Na^+, K^+, and Ca^+ ions of energies ~ 5 keV leads to formation of an n-type surface layer. That is, all the alkali ions including Li^+[89] are donors. It turned out here that the total number of active centers is always small in comparison with the number of ions directed at the surface of the semiconductor. This difference can be at least qualitatively explained by reflection of the bombarding particles (implantation coefficient less than unity), by formation of radiation defects that are predominantly of acceptor type, by cathode sputtering of previously implanted particles, and by desorption of the doping impurity upon heating the specimens.* The electrical conductivity of the doped layer and the distribution profile of the active centers depend on the energy and type of ions, on the direction of bombardment, and on the temperature of the specimen during irradiation. In particular, according to[102], when other conditions remain the same, potassium ions give more donor centers by an order of magnitude than cesium ions do. If the semiconductor is irradiated at room temperature, then the radiation defects will not be able to anneal, and their effect on the electrical conductivity will predominate. Increased temperature suppresses the negative role of the radiation defects. Here we must bear in mind that low-temperature irradiation combined with subsequent annealing is not at all equivalent to bombarding a heated specimen. This involves the fact that point defects can combine into complicated stable complexes when their concentration is high enough.[79] The latter remark agrees fully with the results of the structural studies described in Chapter II.

b) Nitrogen and argon ions. The effect of nitrogen and argon ions on the electrical properties of germanium and silicon has been studied in[87,67,31,32,76,103,104].

Comparison of the damaging action of argon and nitrogen ions on germanium shows[31] that argon ions create radiation defects in greater number than nitrogen ions do, and in a thinner surface layer. This agrees with current ideas on the mechanisms of deceleration of atomic particles in matter. The thickness of the inversion layer formed in n-type Ge by radiation defects increases with increasing dose or energy of the bombarding particles.

It has been shown[76,104] that nitrogen introduced into Ge and Si by ion bombardment is a donor. As measurements of the temperature-dependence of the electrical conductivity and the Hall constant of the nitrogen-doped surface layer showed,[104] the activation energy of the nitrogen impurity in Si is 0.045 ± 0.005 eV. This leads to the idea that nitrogen is a normal donor that occupies substitutional sites.

In order to create an n-type layer near the surface of p-type Si or Ge, it was necessary to anneal at temperatures of ≥750°C and 450°C, respectively, after the nitrogen-ion bombardment. Interestingly, heating of the silicon at >1000°C leads to disappearance of the n-type layer. Perhaps this involves conversion of the nitrogen atoms to an electrically inactive state (e.g., combination into N_2 molecules).

As should have been expected, argon ions implanted into germanium and silicon are electrically inactive.[76]

c) Ions of Group III elements. Doping of silicon by ions of trivalent elements has been studied

*The electrical properties of an implantation defect are determined by its location in the crystal structure. According to the data of [186], 20—25% of the cesium atoms introduced into Si by ion bombardment come to rest in substitutional sites. This can also reduce the utilization coefficient of the impurity.

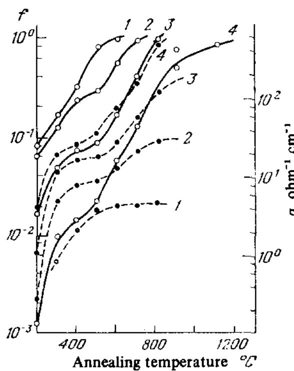


FIG. 10. Relation of the utlization coefficient (solid lines) and the electrical conductivity (dotted lines) of the doped layer to the annealing temperature. Number of boron ions preliminarily directed per cm² of silicon surface is: 1–6.25 × 10^{12}; 2–6.25 × 10^{13}; 3–6.25 × 10^{14}; 4–6.25 × 10^{15}. [105]

in[21,69,92,105-110,193,205] (boron),[30,193,205] (Aluminum),[111,193] (gallium). It has been shown that bombardment combined with high-temperature annealing always leads to appearance of new acceptor levels. Since Group III atoms are acceptors when occupying substitutional sites in silicon, heat treatment was necessary here not only to anneal the radiation defects, but also to transport the implanted particles to active positions.

According to[69,92], when Si is bombarded with B^+ ions, the best results are obtained upon annealing at 600–700°C. Pavlov and his associates[21,105] have studied this problem in greater detail. They found that the temperature needed for annealing increases with increasing dose. This is illustrated by Fig. 10, which shows the relation of the utilization coefficient of the introduced impurity and the electrical conductivity of the irradiated layer to the annealing temperature. The utilization coefficient f is the number of active acceptors per incident particle, and is defined by the formula

$$f=\frac{n_p+N_d}{N_i}, \tag{2}$$

where n_p is the mean concentration of current carriers (holes) in the inversion layer, N_d is the original concentration of donors in the Si, and N_i is the mean concentration of boron atoms introduced by ion bombardment, as calculated under the assumption that the implantation coefficient is unity.

When $N \leq 6 \times 10^{13}\ cm^{-2}$, $f \approx 1$.[105] Further increase in the dose is accompanied by decrease in the utilization coefficient. The authors of[108] have also studied the variation in electrical conductivity during heat treatment of Si layers that had been irradiated by B^+ ions. In particular, they showed that the activation energy of the process is 0.31 ± 0.03 eV at small doses (they assumed that the variation in electrical conductivity results from diffusion of interstitial atoms of the impurity to vacancies with subsequent recombination).

Distribution profiles of active impurities introduced into Si by bombardment by B^+, Al^+, etc., ions have been studied in[107,109,193,205]. I should also mention an attempt to calculate theoretically the depth distribution of implanted atoms (B, Al, P, As) and of radiation defects undertaken* in[112]. The authors of this study showed that the peak in the distribution of implanted particles is farther from the surface than the peak in the distribution of radiation defects.

*Unfortunately, they neglected in [112] the ordered arrangement of the atoms in the crystal. For a calculation of the distribution profile of primary particles captured immediately or after several collisions in linear channels in a crystal structure, see [12].

In[111], they studied the change in electrical properties of silicon resulting from bombardment by Ga^+ ions of energies 20–75 keV. Irradiation was performed at 500°C, and the specimens were annealed for 10 min at 800–900°C after bombardment. The depth distributions of concentration and mobility of the carriers were found from measurements of the surface conductivity and the Hall effect as thin layers were successively removed by etching. It turned out that the number of current carriers initially increases linearly with the dose, but then ceases to vary when their concentration reaches $3 \times 10^{19}\ cm^{-3}$. This corresponds to the limiting solubility of Ga in Si at 900°C. These experiments show that one cannot always attain a concentration of an active impurity exceeding the equilibrium solubility by ion bombardment for all ion-semiconductor combinations.

Doping of germanium with boron, aluminum, and gallium ions has been studied in[113,114]. By comparison with the results obtained upon bombarding Ge with neon, argon, and carbon ions, the authors of[113] convincingly demonstrated the acceptor nature of the levels introduced by B^+ and Al^+ ions. Let us note also a study[115] on doping of silicon with ions of the lanthanides. According to[115], thulium and neodymium ions correspond in Si to deep donor levels having activation energies of ~0.3–0.4 eV.

d) Ions of Group V elements. 1) Phorphorus ions. Doping of silicon with P^+ ions has been studied in[30,69,92,93,108-110,116-118,205-206]. Here the results proved to be analogous in many ways to those that have been obtained by bombarding with boron ions (of course, with the fact taken into account that phosphorus is a donor impurity in Si). In particular, experiments[30] to determine the effect of the annealing temperature on the resistance of the doped layer established that the radiation effects are eliminated and the phosphorus atoms transported to substitutional sites at T ≤ 700–800°C, for doses below 10^3 microcoulombs/cm² (with irradiation at room temperature). Temperatures above 900°C are needed for annealing at large doses. There are indications[69] that the utilization coefficient decreases with increasing dose. Unfortunately, it is hard to compare the results of different studies quantitatively, since the effects being measured are very sensitive to the temperature of the specimen during irradiation and to the intensity of the ion current (rather than simply to the total dose). These important parameters differed appreciably in the studies listed above, and it was not always certain that the authors give the target temperature correctly. (The latter remark applies especially to studies in which high ion-current densities ~10 μA/cm² and above were used; consequently the semiconductor could have been heated considerably by the primary beam.)

The distribution profile of the active impurity in Si doped by 30-keV P^+ ions has been studied in[116] (layer-by-layer etching, combined with measuring the electrical conductivity σ and the Hall effect)* and also

*In [116], in distinction from a number of earlier studies, they took into account in this way the inconstancy of mobility of the current carriers in the doped layers.

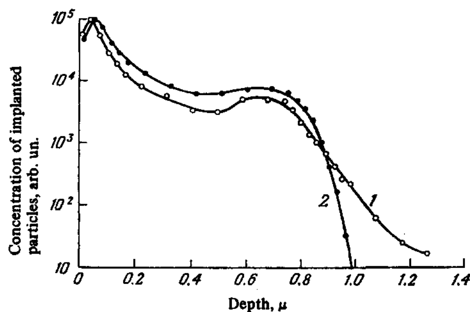


FIG. 11. Depth-dsitribution profiles of phosphorus atoms introduced into Si by ion bombardment. (Irradiation was performed at 77°K in the ⟨110⟩ direction, E = 40 keV, N = 5 × 10^{12} cm^{-2}. The curve 2 was obtained from a specimen that had been irradiated after implanting phosphorus with 40-keV neon ions in an amount N = 10^{15} cm^{-2} at the same temperature. [206]

in[109,117,205]. They demonstrated that the depth distribution of the concentration of current carriers has two regions. In the region closer to the surface, the variations of σ(x) obtained upon bombarding in different directions coincide (the distribution of impurity atoms here is determined by the P^+ ions that have been decelerated in the Si as if in an isotropic substance). The second region is created by ions captured in channels of the crystal structure, and its form depends on the direction of bombardment. This is as yet one of the few methods that permit one to get information on the depth distribution of active impurities. However, we must bear in mind the fact that the relation thus determined of the concentration of electrically-active centers to the coordinate can be distorted, on the one hand, by surface levels at the semiconductor-vacuum boundary, and on the other hand, by the presence of the junction.

Distributions of incorporated particles having two maxima have also been observed repeatedly by other investigators. As an example, Fig. 11 gives some data[206] obtained by bombarding a single crystal of silicon with $_{15}P^{32}$ phosphorus ions of 40 keV energy.

Gusev and Titov[108] have studied in detail the annealing of defects from the change in electrical conductivity of silicon irradiated at room temperature with 30-keV P^+ ions. The annealing was performed for constant times (t = 30 min) in a molybdenum furnace at a residual-gas pressure p = (3–5) × 10^{-5} Torr, and the conductivity of the doped layer was measured by a four-probe method. Figure 12 gives the results obtained in[108]. Upon assuming that the increase in electrical conductivity during annealing mainly occurs because of increasing concentration of electrically-active centers, the authors treated theoretically these processes: 1) decomposition of a complex defect, 2) recombination of two defects due to diffusion, and 3) recombination complicated by the fact that diffusional migration of the most mobile defect is hindered by trapping centers having a high capture cross-section.* It turned out here that, if the annealing time is always the same, and is small, so that the concentration of

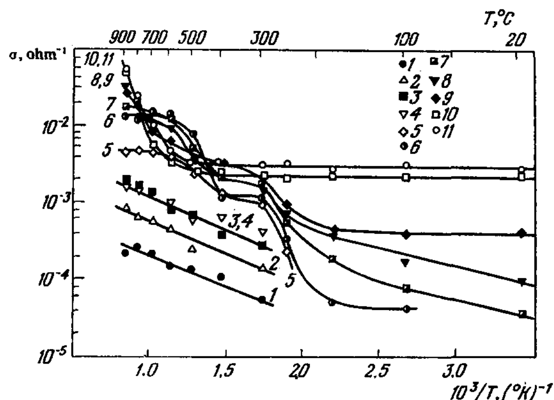


FIG. 12. Variation in the conductivity of the surface layer of silicon doped with 30-keV phosphorus ions. The doses is microcoulombs/cm² are: 1–1; 2–3; 3–10; 4–30; 5–10^2; 6–3 × 10^2; 7–10^3; 8–2 × 10^3; 9–3 × 10^3; 10–6 × 10^3 and 2 × 10^4; 11–2 × 10^5. [108]

electrically-active centers n_e after annealing at the given temperature T appreciably exceeds their initial concentration, then for all three of the mentioned processes,

$$n_e(T) = B\exp\left(-\frac{\Delta E}{KT}\right), \quad (3)$$

where B is a certain constant for each stage of annealing (for small, equal times), and ΔE is the activation energy of annealing. (For processes 1 and 3, the latter equals the activation energy while it is twice the lesser activation energy of diffusion of mobile defects when annealing is determined by process 2.) Hence, under the assumption that the mobility of current carriers does not vary, the authors of[108] obtain

$$\Delta E = -k\frac{d(\ln\sigma)}{d(1/T)}. \quad (4)$$

They established from the data shown in Fig. 12, using Eq. (4), that annealing starts at 300°C for small doses (up to 10^2 microcoulombs/cm²). Here the activation energy of annealing ΔE = 0.172 ± 0.015 eV. They assume that in this case the radiation damage comprises Frenkel' defects, and the increase in the concentration of active centers results from diffusion of interstitial impurity atoms to vacancies with subsequent recombination.

At doses of 3 × 10^2–2 × 10^3 microcoulombs/cm² in the range 200–300°C, another annealing process occurs with a mean activation energy ΔE ≈ 0.5 eV. Since one gets a similar result upon bombarding n-type Si with boron ions, the authors believe that annealing in this stage is due to migration or decomposition of defects that don't contain atoms of the doping impurity. At still higher doses, one observes a third type of annealing in the range T > 600°C. It is characterized by the value ΔE = 0.72 ± 0.25 eV. Annealing in silicon doped by 20-keV phosphorus ions has also been studied in[118]. It was found in this study that annealing occurs in different ways in the regions of the crystal that correspond to deceleration of unchanneled ions and ions captured in channels in the structure (the part of the impurity-distribution profile furthest from the surface). In the former region, the three fundamental stages of annealing corresponded to temperatures of T_1 = 170°C, T_2 = 470°C, and T_3 > 650°C. Only two annealing stages

*A recombination process is understood here to mean any merger of defects that results in forming one electrically-active center.

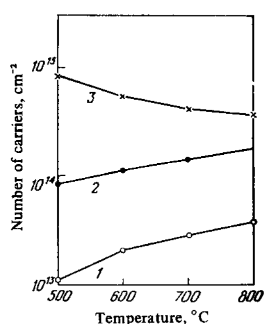


FIG. 13. Variation during annealing in the number of electrically-active centers for Si doped with 20-keV Sb^+ ions at T = 500°C. Curves 2 and 3 correspond to doses respectively 10 times and 100 times as large as for 1. [111]

were detected in the latter region, at 170°C and 330°C. The author of[118] considers that the complex nature of annealing is determined by the variety of defects, some of which can be identified with E-centers (T = 170°C) and A-centers (T = 330°C).

2) Antimony and Arsenic ions. Doping of silicon with Sb^+ and As^+ ions has been studied in detail in[111,193] A merit of this study is that they studied the structural defects introduced into the semiconductor in experiments on α-particle scattering,[58] in parallel with the electrical measurements (electrical conductivity and Hall effect, with layer-by-layer etching). We shall point out as the most interesting result obtained in[111] the fact that the number of electrically-active centers in the semiconductor after ion irradiation increases with increasing annealing temperature when the dose is small, while it declines with increasing temperature at large doses (Fig. 13). Only for antimony ions showed such behavior, and only at high doses, at which the concentration of implanted atoms exceeded the equilibrium concentration. The remaining results of[111] agree with the previously-discussed features of ion doping (annealing of radiation defects in the range 500—600°C, the advantage of "hot" doping, etc.).

e) Doping of films. Smirnov and his associates [22,23,96,120–123] have conducted fundamental studies on the effect of ion bombardment on the electrical properties of films. They used as targets polycrystalline films of CdTe 0.3—0.5 μ thick. They bombarded with cadmium, indium, tellurium, and iodine ions of energies 2—40 keV. They showed from the experiments that In^+ and Cd^+ ions introduce donor-type defects, while Te^+ and I^+ introduce acceptor defects. In a number of cases, the electrically-active centers were apparently not the implanted particles themselves, but associations of them with radiation defects (for indium) or with oxygen (for cadmium). While bombardment by noble-gas ions didn't appreciably change the electrical conductivity of the films, the resistance of the films could be reduced by 3—6 orders of magnitude by irradiation by Cd^+, Te^+, In^+, and I^+ ions. Interestingly, ion bombardment often increased the mobility of the current carriers.

The change in electrical properties of materials upon doping by ion bombardment is determined to a considerable extent by diffusion of the introduced impurities and defects. This can happen both during irradiation and after it has ceased. Consequently, the depth distribution of active centers can disagree with the range distribution of the bombarding particles. The effect of ion bombardment on diffusion of impurities will be discussed in the next section.

3. Diffusion upon Ion Irradiation

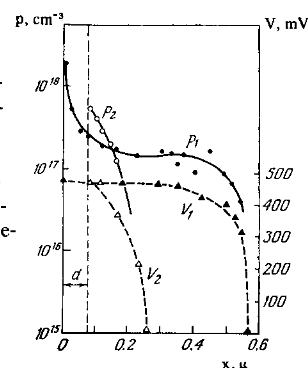
Strack[124] was apparently the first to establish firmly an increase in diffusion coefficients of an impurity upon bombarding semiconductors with ions having energies in the range of interest to us. According to his data, the diffusion coefficients of phosphorus at 820°C in irradiated and unirradiated silicon differed by a factor of 10^5 times! Increased diffusion rates of electrically-active impurities upon bombarding Si with various ions have also been observed in[125–128,74,207,208].

We shall take up separately only the study[128], in which specimens of n-type Si were bombarded at room temperature with 10-keV Al^+ ions in the ⟨111⟩ direction. After irradiation, the crystals were annealed at 800°C for 20 minutes. Then they measured the concentration of current carriers and the photo-e.m.f. at a p-n junction with layer-by-layer removal of material by etching (the curves 1 in Fig. 14). In some cases, they etched away before annealing a surface layer of thickness d = 0.08 μ, which contains the major part of the radiation defects. After this treatment, they obtained the distributions shown in Fig. 14 by the curves 2. This elegant experiment demonstrates very graphically the stimulating action of radiation defects on the diffusion of an impurity (cf. curves 1 and 2 in Fig. 14).

Evidently, the increase in diffusion coefficients upon irradiation is due mainly to generation of vacancies by the bombarding particles and by fast displaced atoms. Under certain conditions, faster diffusion can also arise from formation of dislocations, which are good channels for diffusing atoms.

Nevertheless, ion bombardment can sometimes lead to slower diffusion.[203,206] Let us suppose that the impurity atoms introduced into a semiconductor can migrate both by way of interstices and substitutional sites, with the diffusion coefficient being considerably smaller in the latter case than in the former. Then formation of vacancies in the semiconductor will facilitate transfer of the implanted atoms to substitutional sites. Hence, the number of rapidly diffusing particles will decrease. Apparently, it is precisely these factors that give rise to the differences in the depth distributions of phosphorus ions, as represented

FIG. 14. Variation in the concentration p of current carriers and the photo-e.m.f. V as thin layers of silicon doped with aluminum are removed. Dose N = 10^{15} cm^{-2}. Subscripts: 1—annealing performed after irradiation; 2—after irradiation, a layer having d = 0.08μ was first removed, and then the specimen was annealed. [128]



by the curves 1 and 2 in Fig. 11. Upon being decelerated, phosphorus ions captured in a channel come to rest in interstices. At temperatures below room temperature, such interstitial atoms can still migrate for appreciable distances. This leads to appearance of an exponential region in the depth distribution of the ions (the right-hand part of curve 1 in Fig. 11). If one irradiates the crystal with neon ions after implanting phosphorus, without raising the temperature, then the interstitial phosphorus atoms will be captured by the vacancies that are formed, and the "supertail" in the distribution will disappear (curve 2 in Fig. 11).

4. The Effect of Ion Bombardment on the Behavior of Non-equilibrium Current Carriers

As has been mentioned above, defects introduced into a semiconductor by ion irradiation can serve as effective centers for recombination and capture of current carriers. Consequently, if the rate of generation of carriers is constant, both their steady-state concentration and the number of carriers that recombine at certain particular centers can vary. The latter is essential, e.g., in radiative transitions. There is also a change in the law of time increase (or decay) of the concentration of excess carriers as carrier generation starts (or stops). I shall discuss below some studies in which an effect was observed of ion bombardment on the luminescence and radiation-induced conductivity of semiconductors. Following the suggestion of B. M. Wood, we shall take radiation-induced conductivity to mean the increase in electrical conductivity due to excitation of bound electrons by photons, electrons, ions, or other particles.

a) Radiation-induced conductivity. As a rule, the depth of penetration of ions of energies up to 100 keV into various materials does not exceed 10^{-4} cm.* However, the diffusion distance of current carriers in such semiconductors as Ge and Si is as much as several millimeters. Hence, the effect of ion bombardment on the behavior of excess current carriers can be ascribed to a change in the rate of surface recombination.†

According to[131,132], the transverse radiation-induced conductivity coefficient κ, which is equal to the ratio of the radiation-induced conductivity current to the primary current I_1 upon surface excitation, is defined by the formula

$$\kappa = \frac{K}{S_1 + S}, \quad (5)$$

where S_1 is the rate of surface recombination on the irradiated side of the specimen, S is a constant that depends only on the geometric dimensions of the specimen and the parameters of the semiconductor material, and K is a quantity that depends on these same variables, as well as on the electrical characteristics of the circuit. In addition, the quantity K is directly proportional to the number of electron-hole pairs generated per primary particle.

The only fact of importance to us now is that S_1 enters into neither S nor K. We note that this result was contained implicitly in the earlier studies[133,134]. We see from Eq. (5) that S_1 is inversely proportional to the radiation-induced conductivity coefficient. Hence, the variations of $1/\kappa(N)$ and $S_1(N)$ must be similar. In the very simple case in which the ion bombardment does not affect the curvature of the bands at the surface of the semiconductor, the rate S_1 of surface recombination increases linearly with increasing number of incident ions. Thus it becomes possible to compare quantitatively the efficiency of creation of defects by ions of different types and energies by using the slopes of the experimental straight lines for $1/\kappa(N)$, and also to study the dependence of the rate of defect formation on the direction of motion of the primary ions in the semiconductor crystal, on the temperature, etc. Unfortunately, such experiments have not yet been performed, although the fact itself that $1/\kappa$ varies linearly with the dose has been observed repeatedly upon bombarding germanium with hydrogen and potassium ions.[131,132]

An increase in the rate of surface recombination during ion bombardment and a consequent decrease in the radiation-induced conductivity have been detected for silicon in[28,134,148], and for germanium in[135-141,103,209]. One can again lower the rate of surface recombination by heating the irradiated crystals to 400–500°C[135,139] (in these experiments S_1 varied reversibly in either direction by a factor of 100).

Ion bombardment can also lead to a decrease in the rate of surface recombination. This is sometimes observed with Ge crystals that hadn't been subjected to heat treatment in vacuo after etching. In these cases, the radiation-induced conductivity increases at first (just as in electron bombardment[142,143]). Then it begins to decline for large doses. A decrease in surface recombination upon irradiation with ions and electrons (usually under gas-discharge conditions) is characteristic of $A_{II}B_{IV}$ semiconductors.[144,145,121,122] For example, they observed in[144] an increase in the photoconductivity of CdS crystals by a factor of 10^6 after they had been treated in a gas discharge. The authors explain this by curvature of the bands at the surface in a direction that corresponds to formation of an anti-barrier layer. Consequently, approach of the minority carriers to the surface recombination centers is hindered. Ion bombardment affects the spectral dependence of the photoconductivity, and sometimes extra maxima appear in the photoconductivity spectrum.[122] In[146], negative conductivity was observed in CdSe after irradiation near the intrinsic absorption edge. In[147], generation of electric oscillations was detected in CdSe crystals treated in a gas discharge.

Introduction of recombination centers into the surface layer of a semiconductor alters not only the steady-state value of the radiation-induced conductivity, but also its kinetics. As applied to ion bombardment, this problem has been studied by the authors of[131,149].

*Data on the ranges of ions in amorphous media and in single crystals, as well as on the depth distributions of implanted particles are summarized in [10]. Fundamental theoretical concepts are also presented there, as well as some formulas for calculation.

†The rate of surface recombination is equal to the ratio of the number of recombination events per unit time per unit of surface to the concentration of non-equilibrium carriers near the surface outside the space-charge region. The conditions under which this concept can be introduced have been discussed in detail in [129,130].

Even earlier, the kinetics of photoconduction under unsymmetrical boundary conditions was treated in detail in[150]; see also[151].

After a long enough time has elapsed after carrier production has ceased, the decline in radiation-conductivity current will follow an exponential law with a time constant τ_1, which is defined by the condition

$$\frac{1}{\tau_1}=\frac{D\alpha^2}{a^2}+\frac{1}{\tau_0}; \qquad (6)$$

Here a is the thickness of the homogeneous, rectangular semiconductor plate, D is the diffusion coefficient, and τ_0 is the volume lifetime of the minority carriers. The value of α depends on the rate of surface recombination on the irradiated and opposite sides of the semiconductor (S_1 and S_2, respectively), and it can be found from the equation

$$\operatorname{ctg}\alpha=\frac{D}{a(S_1+S_2)}\left(\alpha-\frac{a^2S_1S_2}{D^2\alpha}\right). \qquad (7)$$

One can determine D, τ_0, and the initial rate S_p of surface recombination by measuring the value of τ_1 for three states of the target:

a) the specimen is not subjected to ion bombardment ($S_1 = S_2 = S_p$);

b) the surface layer is substantially damaged by ions on one side ($S_1 \gg S_p = S_2$);

c) both sides of the target are damaged by ions (S_1, $S_2 \gg S_p$). After this, by using Eqs. (6) and (7), one can easily construct the theoretical relation $\tau_1(S_1)$ for the given a, D, τ_0, and S_p. One can find $S_1(N)$ by comparing the function $\tau_1(S_1)$ with the experimental relation of τ_1 to the number N of ions incident per cm^2 of one of the surfaces of the specimen. Figure 15 gives the functions $\tau_1(N)$ and $S_1(N)$ obtained in[139,149] upon bombarding a single crystal of germanium with 8-keV potassium ions. We see from the graph that S_1 increases linearly with the dose (this had been noted above in discussing Eq. (5)). As determined from the data of Fig. 15, the value of the overall recombination cross-section for all defects created in the surface layer of the semiconductor per incident particle proved to be 10^{-16} cm^2.

One can also get important information on the properties of defects that are introduced into a semiconductor by ion bombardment by studying the field effect, the frequency-dependence of the photoconductivity, the contact potential difference, etc.[141,152,209] In particular, they established in[141] that He^+, N^+, and Ar^+ ions of 50 keV energy not only increase the rate of surface recombination, but they also alter the shape of the dependence of S_1 on the surface potential. Upon irradiation, the surface potential and the total surface charge become (in the small-dose range) more and more

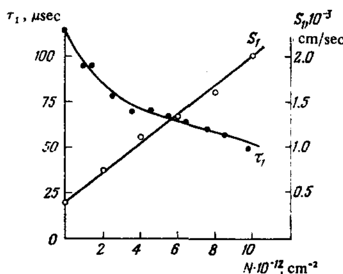


FIG. 15. Relation of the time constant τ_1 for decay of the radiation-induced conductivity current and the rate S_1 of surface recombination to the dose upon bombarding a single crystal of germanium with potassium ions. E = 8 keV, T = 300°K, ⟨110⟩. [131,149]

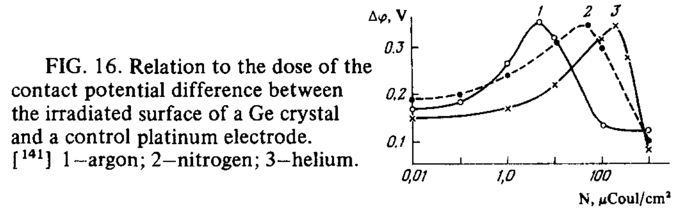


FIG. 16. Relation to the dose of the contact potential difference between the irradiated surface of a Ge crystal and a control platinum electrode. [141] 1—argon; 2—nitrogen; 3—helium.

negative with increasing numbers of incident ions. This corresponds to introduction of radiation defects that are mainly of acceptor type. The relation obtained in[141] of the contact potential difference to the dose is given in Fig. 16. We see that the damaging power of ions increases with the atomic number, in full accord with the theoretical ideas and the results of earlier observations.[139,152]

Experiments on the field effect performed on n-type Ge crystals irradiated in a glow discharge with helium ions have shown[209] that ion bombardment leads to appearance of a discrete energy level in the forbidden band. The capture cross-sections for holes and electrons for this recombination center were estimated to be 10^{-14} cm^2 and 10^{-15} cm^2, respectively.

An effect was found in[33] of ion-bombardment on the spectral dependence of the change in contact potential upon illumination.

b) Luminescence upon bombarding with electrons and ions. The deterioration of luminescent properties of phosphors resulting from ion bombardment (aging) is generally known (see, e.g.[153-156]). It has also been established that the intensity of emission upon ion bombardment declines according to the law[153]

$$I=\frac{I_0}{1+CN}, \qquad (8)$$

Here I_0 and I are respectively the initial and final luminescence intensities, N is the dose, and C is a certain constant for a given phosphor that depends on the type of ions. The deterioration constant C, and hence also the rate of damage, increase with increasing mass of the bombarding particles.

However, it wasn't clear until recently how the deterioration constant was related to the parameters of the luminophor. The studies of Makarov[157,158] and of Wijngaarden and Hastings[159] have thrown some light on this problem. In[157,158,160], they studied the variation in luminescence of single crystals of silicon carbide when bombarded by hydrogen and lithium ions of 4–16 keV energy. Figure 17 shows some typical results. The author of[157,158] treated the high-dose region, where the ionoluminescence intensity is in-

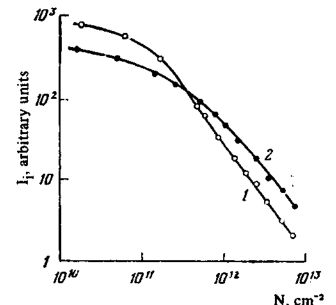


FIG. 17. Relation to the dose of ionoluminescence intensity of SiC upon bombarding with 10-keV protons. λ(Å): 1–4700; 2–5200. [160]

versely proportional to the number of incident ions, and assumed that the depth R of penetration of ions in this region appreciably exceeds the diffusion distance of the current carriers (the decline in luminescence results from variation in the bulk concentration of centers for radiationless recombination within the layer of thickness R). Thus he found an expression for the deterioration constant in the following form:

$$C = \frac{\tau_0 N_c \sigma v f(\varphi)}{R}, \quad (9)$$

Here τ_0 is the lifetime in the original specimen, N_C is the number of capture centers created per ion, σ is the capture cross-section, v is the thermal velocity of the carriers, and $f(\varphi)$ is a function of the ratio $\varphi = R/L_0$ of the penetration depth to the diffusion distance in the original specimen. This function takes into account radiationless recombination at the surface. Equation (9) was derived under the assumption of a uniform distribution of defects in the damaged layer. The latter is apparently a good enough assumption for light, strongly-scattered particles. By using Eq. (9), he could establish that in SiC the overall cross-section per proton for capture of current carriers by the radiation-defect levels is practically independent of the proton energy over the range 4–16 keV. This cross-section amounts to $(6-7) \times 10^{-15}$ cm^2.

A formula analogous to (9), but written in a somewhat different form and not taking account of surface recombination, was also derived in[159]. In the same study, they undertook an attempt to find the depth distribution of radiation defects. For this purpose, they subjected a ZnO: Zn luminophor to preliminary damage by 102-keV helium ions. Then they studied the relation of I/I_0 to the energy of probing He^+ and Ar^+ ions in the range 5–100 keV. It turned out that this ratio is constant throughout the studied range, and is the same for the two ions. Hence, in particular, one should conclude that the depth distribution of the radiation defects is uniform. One can also get information on the spatial distribution of defects in experiments in which the irradiated layers are probed with electrons of varying energies.[157,162] As was shown in[161], one can find the total energy losses upon passage through a a thin non-luminous layer by damaging a luminophor by slow ions and probing with faster ones.

In connection with the data depicted in Fig. 17, I should point out that the intensity of emission is not proportional to N^{-1} for all wavelengths at large doses. This involves the fact[157,160] that the spectral composition of the emission also varies upon ion bombardment of SiC. Consequently, the course of curve 2 in Fig. 17 is more complex, since an increase in intensity resulting from appearance of new luminescence centers is imposed on the decline in emission arising from defect formation.

Changes in the luminescence spectra of single crystals of silicon carbide due to ion bombardment have been studied in[157,162,163]. Figure 18 shows some typical results. As these data show, ion irradiation combined with subsequent heating leads to an overall increase in emission and to appearance of a new band in the luminescence spectrum.

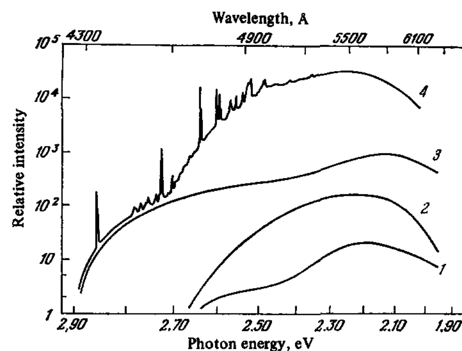


FIG. 18. Cathodoluminescence spectra of silicon carbide. 1 and 2–unirradiated specimens; 3 and 4–specimens after bombardment with K^+ ions and heating to 1200°C. Curves 1 and 3 are for 300°K, 2 and 4 for 80°K. The fine structure has been omitted from curve 2 for simplicity. [163]

Figure 19 shows on a larger scale the fine structure of the emission spectra that arose after bombardment and annealing.[162] For convenience, the curves corresponding to different modifications of SiC are shifted along the energy axis to make the first lines of the fine structure coincide. The spectra shown in Fig. 19 can be represented as a combination of several series. The head line of each series is denoted by the letters A, B, and C. The same letter symbols are given to the rest of the lines of each series. The subscripts (e.g., A_{70}) indicate the energies in milli-electron volts of the phonons that must be emitted simultaneously with the photon in order to obtain longer-wavelength emission instead of the head line. We see from Fig. 19 that the phonon energies are about the same for all the modifications. I should note especially that the half-width of the head lines in the series A, B, and C at 80°K is less than kT.

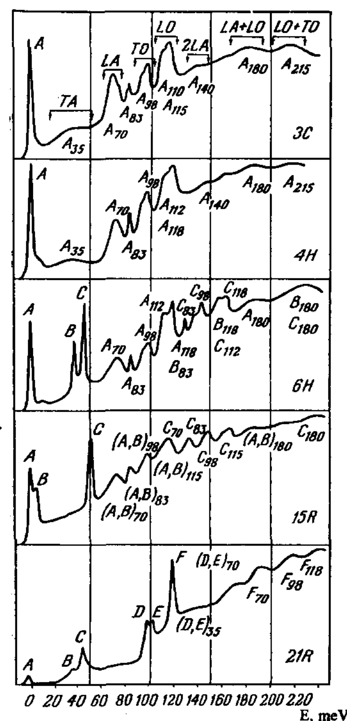


FIG. 19. Fine structure of the luminescence spectra of SiC crystals of different modifications after ion irradiation and heating to 1100°C. The energy in meV as measured from the first line is plotted along the axis of abscissas. The spectra were taken at 80°K (data of [162]).

In[157,162,163], they also studied the change in the spectra owing to irradiation by fast neutrons and electrons having E ~ 2 MeV. Here they found that the luminescence spectrum after heating does not depend on the type of primary particles (alkali or gas ions, neutrons, electrons). Thus, the radiation defects in SiC responsible for radiative recombination processes proved to be identical in all cases. Study of luminescence spectra makes it possible to get information on the location on the energy scale of the levels belonging to defects and on the nature of these defects.[157,162] A highly valuable characteristic of the luminescence method is that this method of studying structural damage introduced by ion bombardment has considerably higher sensitivity, at least for a number of objects, than the methods based on measuring electrical conductivity or optical absorption.

IV. EFFECT OF ION BOMBARDMENT ON THE OPTICAL AND CERTAIN OTHER PROPERTIES OF SEMICONDUCTORS

Introduction of defects into semiconductors by ion bombardment is accompanied by appearance of local energy levels in the forbidden energy gap. Naturally, this must primarily affect the optical properties of the material in the region of photon energies less than the width of the forbidden band. I have mentioned above the change in the luminescence, absorption, and photoconductivity spectra upon ion irradiation. To supplement this, I should mention the studies of photoluminescence of CdS, ZnS, and ZnTe crystals[115,164,210] and of the optical properties of diamonds.[165,166,211]

In[115,164], photons emitted by excited Nd^{3+} ions replacing Cd^{2+} at crystal-structure sites were detected in the photoluminescence spectrum of CdS after bombardment by neodymium ions. Nevertheless, the corresponding spectral lines could not be detected in ZnS crystals. The authors of[115] tend to explain this by the large dimensions of Nd atoms as compared with Zn. Consequently, the former very rarely replaces zinc at structural sites. The authors of[210] observed the photoluminescence of oxygen introduced into ZnTe by ion bombardment.

I shall mention also[212], which reports the results of studying divacancies that appeared in silicon after irradiation by 400-keV oxygen ions from an optical absorption band characteristic of them at $\lambda \approx 1.8\ \mu$.

Since ion bombardment can lead to a considerable change in the electrical conductivity of semiconductors, the optical properties of the material should be altered in the infrared, where the cross-section for interaction of light with free carriers is especially large. This fact was used in[167], whose authors undertook an attempt to study the concentration distribution of free carriers in silicon doped with phosphorus ions from the change in the infrared reflection coefficient with layer-by-layer etching.

For information on the effect of ion bombardment on the external photoelectric effect of semiconductors, see, e.g.[39].

However, not all changes in optical properties can be explained simply as resulting from formation and accumulation of local energy levels in the forbidden band of the semiconductor. In[168], spectral modulation of infrared absorption (Fig. 20) was observed upon bombarding Si with protons and helium ions of energies E ~ 100 keV and higher. The location of the peaks in the spectral dependence of the absorption coefficient was determined by the energy of the ions alone, and their amplitude increased with increasing dose. The authors of[168] think that a "discontinuous gas layer" is formed at the end of the range of the primary particles by capture of the helium or hydrogen by the crystal. From this standpoint, the peaks in Fig. 20 result from interference of the waves reflected from the face of the specimen and from the boundary between the irradiated and non-irradiated regions of the crystal. High-temperature annealing diminished the amplitude of the peaks only at T ≥ 1150°C. However, even heating to 1400°C proved insufficient to eliminate completely the changes produced by ion bombardment.

An increase in the reflection coefficient, the refractive index, and the absorption coefficient were observed in[165] upon bombarding diamonds with 20-keV carbon ions. It was noted that annealing at 760°C for 30 min restores the original properties (for doses $N \leq 2 \times 10^{15}\ cm^{-2}$). Changes in the refractive index owing to ion irradiation are also reported in[166,211,213]. By studying the spectral dependence of the intensity of reflected light for diamond crystals irradiated by Li^+, B^+, and P^+ ions having E = 20–120 keV, the authors of[166] got information on the distribution of radiation defects from curves analogous to those shown in Fig. 20.

A color change in single crystals of Si upon bombardment with phosphorus, boron, antimony, neon, xenon, and silicon ions has been observed in[169,111,18,19]. According to[18,19], a trace of the beam that is visible to the naked eye appears on the surface of the silicon after ion irradiation. The color depends on the type of ions, on their energies, and on the dose. At high doses, the surface acquires a milky shade. In all probability, this effect results from Rayleigh scattering of the incident light by disordered regions. The scattering probability depends on the frequency of the photons, the scattering angle, and the thickness of the scattering layer.[18] Figure 21 shows the relation of the intensity of scattered light to the photon energy that was calculated in[18]. As we see from Fig. 21, the color of the spot produced by the ion beam should depend on the thickness of the damaged layer. Transition to a milky shade occurs when the number of disordered regions is so large that multiple scattering becomes possible.

Annealing at 650°C for an hour restores the color of the crystal. As fast-electron diffraction and proton-

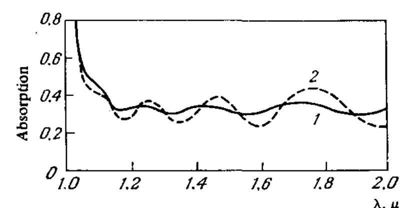


FIG. 20. Wavelength-dependence of absorption after irradiating Si with 130-keV protons. Doses (coulombs/cm²): 1–0.043; 2–0.17.

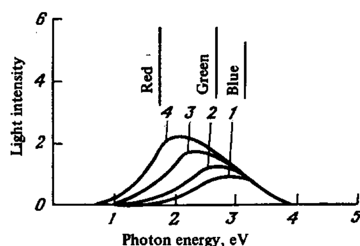
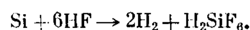


FIG. 21. Relation of the light-scattering intensity to the photon energy (theoretical data). The angle between the normal to the surface and the direction of propagation of the scattered light is 45°; the thickness R of the scattering layer in Å is: 1–1000; 2–2000; 3–5000; 4–10,000. [18]

scattering experiments show, crystallization of the amorphized layers of the silicon occurs simultaneously with this. As we should have expected from the mechanism of color change described above, it takes a larger dose of ions to get a milky shade with higher temperatures of the crystal and when the conditions for channeling of the ions are better fulfilled.

In this same section, we shall treat the change in chemical activity of semiconductors resulting from ion bombardment. Of course, this property is not related directly to optical processes. I can justify combining them in one section only by the fact that all these problems have been poorly studied.

Disordered crystal structure of solids is accompanied by weakening and rupture of the chemical bonds between atoms. The chemical activity of the substance is consequently increased. Increased rates of solution of Ge and Si in etching agents after ion bombardment have been observed in[28,19,214]. As we known, silicon does not dissolve in hydrofluoric acid. However, after the surface layer of Si has been rendered amorphous with ions, according to the data of[28,19,214], it could be removed by etching with HF. According to[19], a reaction occurs here with evolution of hydrogen:



$$Si + 6HF \rightarrow 2H_2 + H_2SiF_6.$$

Whenever the course of a reaction is limited by diffusion, as the previous section implies, ion bombardment should accelerate chemical processes, owing to increased rate of supply of the reagent.

Ion irradiation can lead to alteration of an entire series of other properties of semiconductors, e.g., a change in thermoelectric emission of an oxide cathode,[170-172] or a loss of hardness of materials.

One can also become acquainted with certain problems of ion doping of semiconductors in[215-217].

V. CONCLUSION

Although the problem of the effect of ion bombardment on the properties of semiconductors is relatively new, the number of published articles on these problems is already measured in three digits. However, this does not mean that the phenomena discussed above have been studied well and fully enough. Apparently, most of the studies along this line still lie in the future.

To conduct this cycle of studies absolutely requires the creation of specific methods for checking on the structure and electrical and optical properties of the surface layers of a semiconductor. Several new, original methods have already been proposed. However, as a rule, one can only use them as yet to get qualitative results, since the theoretical bases of the methods have not been developed, and their sensitivities have not been compared. More attention should also be paid in the future to revealing the general laws of behavior of radiation defects produced by ions and highly penetrating radiation (γ-rays, fast electrons, and neutrons).

The results of the experiments discussed in this review show that by ion bombardment one can not only alter in a controlled way the parameters of semiconductors, but one can also get materials with properties that can't be attained by using other technological means. Consequently, along with solving varied applied problems, studies along this line should facilitate the development of solid state physics and the physics of semiconductors.

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