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THE NATURE AND ENERGY SPECTRUM OF RADIATION DEFECTS IN SEMICONDUCTORS

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1. INTRODUCTION

INVESTIGATIONS of radiation defects in single crystals of covalent semiconductors soon led to the conclusion that the simple models and representations of the energy spectrum of levels due to a random distribution of separated "Frenkel pairs" in a crystal are almost always complicated by the processes of the migration and interaction of primary defects with impurities or defects originally present in the crystal.

Sensitive methods—for example, studies of the structure of the photoconductivity spectra—have shown that sometimes irradiated crystals may contain staggeringly large numbers of local levels.

Owing to the use of spin resonance techniques and the combination of low-temperature irradiation with optical and electrical measurements, our ideas about the nature and energy spectrum of radiation defects in covalent semiconductors have now become much clearer. Recently, it has become possible to experiment with crystals (for example, germanium) in which the concentration of electrically active impurities is sufficiently low (about 10^{12} cm^{-3}) so that at relatively moderate defect concentrations (for example, 10^{14} cm^{-3}) the number of probable complexes with impurities remains relatively small. New opportunities are offered by experiments on dislocation-free crystals.

The relative advantages of the optical and photoelectric measurements in the study of semiconductors are now sufficiently well known, and their application to investigations of radiation defects have been discussed in an excellent article by Fan and Ramdas.^[1] Attention should be drawn to the peculiarity which sometimes greatly hinders the comparison and interpretation of the data on the absorption and photoconductivity spectra: in order to detect the absorption in crystals of moderate thickness, it is necessary to have a local level concentration on the order of 10^{16} cm^{-3} . Such concentrations are reached at relatively high doses of hard radiation, when the primary process of structural-defect formation is necessarily accompanied by important secondary phenomena due to the migration of point defects, their interaction, and complex formation. As shown in our earlier work, the energy-spectrum structure of silicon containing a large number of defects becomes blurred so that many of its characteristic features disappear.^[2] Therefore, in spite of certain advantages of the optical-absorption method, among which is the possibility of direct ob-

servation of electron transitions to the excited state, it is often difficult to compare and present within one model of a process the data on the absorption in highly defective crystals and the photoconductivity data.

2. ENERGY SPECTRUM OF LOCAL CENTERS IN SILICON IRRADIATED WITH FAST ELECTRONS

Between 1957 and 1962, detailed experimental studies established the nature of the recombination centers appearing in very high concentrations when silicon, containing oxygen and donor impurities, is exposed to hard radiation. It has been shown that the A-centers, with an energy level near $E_C - 0.16 \text{ eV}$,* consist of oxygen impurity atoms associated with vacancies, and that the centers with a deeper level consist of vacancies associated with a donor impurity (the E-centers). With phosphorus as an impurity, the E center level was found to be near $E_C - 0.40 \text{ eV}$. The method of electron spin resonance has played a particularly important role in the interpretation of the space symmetry of these centers and the final determination of their complex nature.^[14,32]

Investigations of the photoconductivity of irradiated silicon, carried out by Fan and Ramdas,^[3] as well as by A. F. Plotnikov, V. D. Tkachev, and the present author,^[2,4,5,10] have confirmed the information about the positions of the levels in the A- and E-centers. Experiments with low-temperature irradiation have shown that the "primary" photoconductivity spectrum has no structure and probably represents an assembly of Frenkel pairs with different distances between the interstitial atom and the vacancy.

In addition to the levels corresponding to the A- and E-centers, the photoconductivity spectra have been found to have particularly well-defined structure at relatively low integral radiation doses. The coincidence of some of the steps in this "second-order intensity spectrum" with the positions of the levels of several typical residual impurities has made it necessary to carry out special experiments on the irradiation of very pure silicon and of silicon into which the suspected impurities were introduced deliberately. We shall consider first the data from the photoconductivity measurements carried out on silicon grown under special conditions and containing oxygen in concentra-

* E_C is the energy corresponding to the bottom of the conduction band; E_V is the energy corresponding to the top of the valence band.

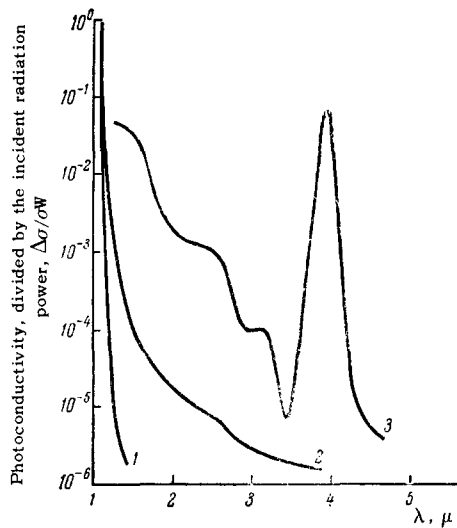


FIG. 1. Photoconductivity spectra of a very pure p-type silicon single crystal containing not more than 10^{14} cm^{-3} of oxygen and having a resistivity of 9500 ohm-cm before irradiation (measurements at about 100°K). 1) Before irradiation; 2) after irradiation with a flux of 2×10^{15} cm^{-2} 1-MeV electrons; 3) silicon containing about 10^{16} cm^{-3} oxygen atoms and boron acceptors, after irradiation with the same electron flux.

tions which, according to indirect estimates, did not exceed 10^{14} cm^{-3} , as well as chemical impurities (with deep levels), in concentrations which were below the levels detectable by electrical methods. The investigated single crystals were p-type before irradiation; at room temperature, their electrical resistivity was 9500 ohm-cm and their nonequilibrium carrier lifetime about 1 msec. The main new result, showing a basically different characteristic of the effect of electron irradiation of such silicon, was the absence of a discrete structure corresponding to the A- and E-centers and to the levels of residual impurities (in our earlier experiments, these were primarily copper and gold^[6]). The photoconductivity spectrum of one such sample is shown in Fig. 1, where it is compared with a typical spectrum for "normal" p-type silicon. The structureless photoconductivity region, concentrated mainly near the fundamental absorption band edge but extending to 4μ , may be associated with the levels of pairs of point defects separated by considerable distances.

This structureless region appears immediately after irradiation at room temperature or at liquid nitrogen temperature, and, in the latter case, no discrete structure appears after heating to room temperature. In contrast to the cited results, obtained for very pure crystals, the large number of "steps" found systematically in the photoconductivity spectra of "normal" silicon irradiated with sufficiently low integral radiation doses^[2,4] is partly related to the residual impurities. Some of the steps in the photoconductivity spectra agree well with the values of the corresponding deep gold and copper levels, deter-

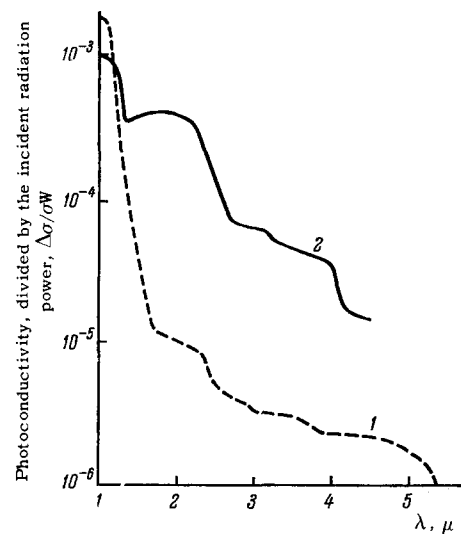


FIG. 2. Photoconductivity spectra of copper-doped silicon before and after irradiation with a flux of 2.5×10^{17} electrons/ cm^2 (1 MeV). 1) Before irradiation, at 100°K ; 2) after irradiation.

mined independently of the data on the temperature dependence of the Hall emf and electrical conductivity, or determined from recombination experiments. The experiments on unirradiated silicon crystals containing, in some cases, the deliberately introduced gold and copper, and in other cases, the same elements as the residual impurities, made it possible to establish that, in the test samples grown by the method of zone melting in vacuum without the use of a crucible, gold was present in concentrations of 10^{10} – 10^{11} cm^{-3} and copper in concentrations of 10^9 – 10^{10} cm^{-3} . Silicon grown in quartz usually contained 10^{11} – 10^{12} cm^{-3} electrically active gold atoms.^[6]

Initially, it was assumed that irradiation with fast electrons or other forms of hard radiation, which increases the resistivity of silicon, gives rise, first of all, to more favorable conditions for the observation and resolution of the structure in the photoconductivity spectra associated with the residual impurities. A more careful examination has shown that the irradiation with fast electrons also produces a sharp relative rise of the "steps" in the spectra associated with the copper and gold levels in silicon.^[7] Figure 2 gives a comparison of the spectra for copper-bearing silicon samples before and after irradiation with 2.5×10^{17} electrons/ cm^2 (1 MeV energy). Curve 1 represents the photoconductivity spectrum of an unirradiated sample containing about 10^{15} copper atoms/ cm^3 at 100°K . Curve 2 represents the same sample after irradiation.

The rise in the photoconductivity signal in the 2.8μ region is associated with electron transitions from the valence band to the copper acceptor level $E_V + 0.49$ eV, while the rise in the 5.3μ region is associated with the copper donor level at $E_V + 0.24$ eV.^[8] The small steps near 3 and 3.75μ are possibly associated with the presence of a zinc impurity ($E_V + 0.4$ eV) or

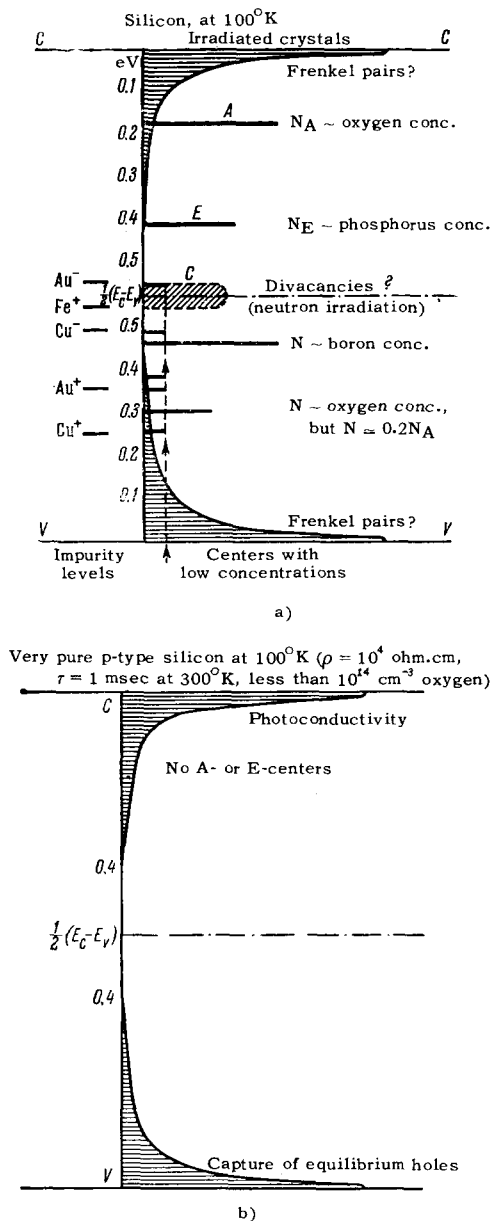


FIG. 3. Energy levels of some impurities in silicon (on the left) and of centers observed after electron or neutron irradiation. a) "Normal" Si; b) very pure Si.

a gold impurity ($E_V + 0.35$ eV) in the original material.

It is evident from curve 2 that, after fast-electron irradiation, the step associated with the copper acceptor level $E_V + 0.49$ eV has become much more pronounced. Numerical estimates have shown that the density of levels has risen by a factor of 4–5.

We may assume that point defects (probably vacancies) produced by irradiation give rise to an increase in the concentration of copper atoms in the electrically active state,* i.e., the irradiation "activates" the

*We mean the states with deep energy levels. We are not considering the energy levels of copper at interstices.

chemical impurity. Similar results have been obtained for silicon samples doped with gold.

The dependence of the concentration of electrically active copper in germanium on the number of vacancies was mentioned in the work of Fuller and Ditzemberger,^[9] who discovered that in deformed samples the rate of saturation with electrically active copper is considerably higher than in undeformed samples. This is obviously related to the appearance, apart from dislocations, of a large number of vacancies due to plastic deformation. A comparison of the photoconductivity spectra and an analysis of the kinetics of the photoconductivity signal rise (which has made it possible to determine the cross section for carrier capture by individual levels,^[2]) has led to the conclusion that some of the levels not identified earlier in irradiated p-type silicon are associated with "activated" impurities.

The $E_V + 0.24$ eV and $E_V + 0.35$ eV levels represent the donor levels of copper and gold, respectively. The $E_V + 0.49$ eV and $E_C - 0.54$ eV levels represent the acceptor levels of the same two impurities. Probably, some other levels, generated in low concentrations by the irradiation of silicon, also appear due to the increase in the concentration of electrically active impurity centers, brought about by the interaction with vacancies. Figure 3 shows the energy positions of the centers observed in irradiated silicon, as well as the ionization energies of various impurities.

It is worth noting that the center having a level near $E_C - 0.55$ eV has certain characteristics which support the suggestion of Bemski, Szymanski, and Wright^[11] that in this case we are observing an effect associated with divacancies or other complexes consisting of several simple defects. Comparison of the photoconductivity spectra of crystals irradiated with 1 MeV electrons and weak fast-neutron beams has shown that, in the latter case, the relative rate of generation of the centers with the $E_C - 0.55$ eV level is an order of magnitude higher. Moreover, in experiments on the neutron irradiation (at sufficiently high doses) of silicon containing a known amount of gold, the concentration of the generated centers with the $E_C - 0.55$ eV level was greater than the concentration of gold atoms. Therefore, we may assume that the positions of the levels of complicated complexes (probably divacancies^[11]) and gold in the forbidden band are approximately the same.

The scheme shown in Fig. 3 illustrates some of the conclusions arising out of studies of the dependence of the energy spectrum of local levels in irradiated silicon on the impurity content.

3. RADIATION DEFECTS IN LITHIUM-DOPED SILICON

Lithium atoms introduced into silicon migrate easily along the interstices and interact actively with other impurities and defects. A lithium atom in an

interstice in the silicon lattice represents a shallow donor level with an ionization energy of 0.033 eV. LiO^+ complexes, stable at room temperature, and representing shallow donor centers, appear in oxygen-containing silicon.^[12] It has been suggested that the processes of the interaction of lithium, introduced first into the silicon, with subsequently produced radiation defects, should be very simple to analyze. In experiments carried out at Moscow State University, by I. V. Smirnova, V. A. Chapnin, and the present author, lithium was introduced by thermal diffusion from a tin-lithium alloy at 550–650°C into p-type silicon, which had been grown in quartz crucibles and contained boron (acceptor) and oxygen. After thermal diffusion, the samples acquired n-type conduction with an electron density ranging from 3×10^{14} to $2 \times 10^{17} \text{ cm}^{-3}$. The irradiation was carried out at the Physics Institute of the USSR Academy of Sciences using 0.9 MeV or 1 MeV electrons at room temperature, or reactor neutrons at about 60°C. The energy spectrum of the defects and its change on annealing were determined from the data on the temperature dependence of the concentration found from measurements of the Hall effect and the electrical conductivity.^[13]

The samples containing lithium donors, in excess of 10^{17} cm^{-3} , and irradiated with electrons, exhibited a system of relatively shallow levels near the bottom of the conduction band. According to Hall emf data, there were few A-center levels at the depth of $E_C - 0.16 \text{ eV}$. On the other hand, electron bombardment produced A-centers in crystals with an equilibrium electron density less than 10^{16} cm^{-3} . However, in the latter case, the efficiency of the A-center generation was only 0.04 cm^{-1} compared with 0.1 cm^{-1} in n-type silicon having phosphorus as a donor and containing the same amount of oxygen. The same difference was observed by Watkins et al.^[14] Bearing in mind the formation of LiO^+ complexes, we may assume that in samples with a sufficiently high concentration of lithium (more than 10^{17} cm^{-3}) there were few residual oxygen atoms free to interact with vacancies and to form the A-centers.

As mentioned in connection with the analysis of the photoconductivity spectra, including recent measurements on very pure silicon, the most obvious conclusion is to ascribe the relatively shallow electron-capture levels to Frenkel pairs with different separations between the interstitial atom and the vacancy.

The data on the "displacement" of the edge of the strong optical absorption region does not contradict this suggestion. Unfortunately, even at helium temperatures, it is not possible to resolve the structure in this region, which corresponds to discrete types of transition from the valence band to local levels.

Short-duration (10 min.) heating to 70°C of samples irradiated with electrons and having a concentration of Li donors of the order of 10^{17} cm^{-3} , reduced appreciably the equilibrium electron density (Fig. 4). This

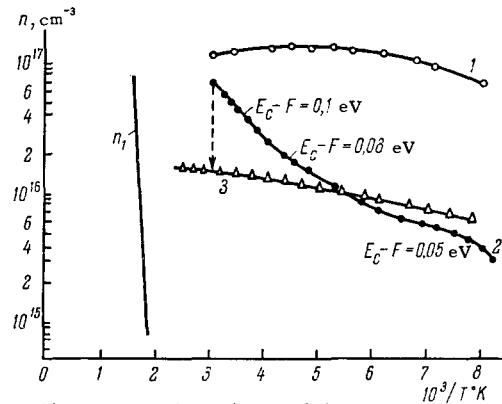


FIG. 4. Temperature dependence of the carrier density in silicon. After the diffusion of lithium at room temperature, the electron density was $1.5 \times 10^{17} \text{ cm}^{-3}$. 1) Before irradiation; 2) after irradiation with a flux of $2.4 \times 10^{17} \text{ cm}^{-2}$ 0.9-MeV electrons; 3) after the precipitation of lithium at radiation defects at 70°C (10 min).

reduction in the density was ascribed by Smirnova, Chapnin, and the present author^[15] to the interaction of lithium ions and radiation defects, i.e., the precipitation of lithium. Obviously, lithium precipitates at a defect in the form of an atom and, therefore, the equilibrium electron density in the conduction band decreases but the existence of new complexes (for example, lithium atoms with vacancies) does not affect the temperature dependence of the Hall effect.

Simultaneously with the reduction in the electron density in the conduction band, the electron capture levels at $E_C - 0.16 \text{ eV}$, due to the A-centers, disappear. The process of lithium precipitation at radiation defects also takes place at room temperature but much more slowly. This is because in oxygen-bearing silicon the rate of diffusion of lithium at low temperatures is limited by its interaction with oxygen. The effective diffusion coefficient of lithium ions is

$$D_{\text{eff}} = D_0 \left(1 + \frac{[\text{O}]}{C} \right)^{-1}, \quad (1)$$

where D_0 is the diffusion coefficient for a crystal free of oxygen, $[\text{O}]$ is the concentration of oxygen, and C is the constant of the reaction



D_{eff} is approximately 100 times smaller than D_0 , at room temperature, for oxygen concentrations of about 10^{17} cm^{-3} . A rise of temperature by 60–70 deg increases D_{eff} by a factor of 50–100 and the process of the interaction with defects is accelerated. At these temperatures, lithium ions diffuse faster than vacancies.

The interaction of lithium with simple radiation defects, detected in fast electron experiments, makes it possible to interpret the earlier results on the irradiation of silicon, containing $(2-8) \times 10^{16} \text{ cm}^{-3}$ lithium, with fast neutrons in a reactor (neutron fluxes from 5×10^{16} to $5 \times 10^{17} \text{ cm}^{-2}$). The temperature in the reactor reached 70–80°C. The observed changes in the

irradiated samples were limited to a reduction in the conduction electron density; no levels were detected in the interval 0.05–0.23 eV from the bottom of the conduction band. Obviously, lithium ions managed to precipitate at defects during irradiation, so that the defects could not move further in the crystal.

Initially, Smirnova, Chapnin and the present author^[15] used the theory of precipitation from a super-saturated solution, which postulated the formation of aggregates of the precipitated particles, to analyze the kinetics of the interaction of lithium with radiation defects. However, it was found that even after precipitation the concentration of “lithium” donors remained higher than the equilibrium concentration at a given temperature. This forced us to assume that only one ion of lithium interacted with one defect. Such a process is analogous to the annealing of simple defects by the annihilation of an interstitial atom and a vacancy, with the difference that here the vacancy interacts with a lithium ion.

According to this assumption, the number of lithium ions precipitated at vacancies should be equal to the reduction in the electron density in the conduction band. Using the theory of the annealing of “heterogeneous” defect pairs, we can write the expression for the fraction of defects which have interacted up to time t :

$$1 - f(t) = \frac{1}{1 + 4\pi r_{\min} D C_A^0 t}, \quad (3)$$

where t is the annealing duration, r_{\min} is the radius of capture at which a “particle” forms a complex, D is the sum of the diffusion coefficients of the “particles”, C_A^0 is the initial concentration of the “particles.” Comparison of the theory with experiment made it possible to determine the capture radius, which was found to be 5.4×10^{-8} cm. This value is close to the lattice constant of silicon.

It was discovered that the type of conduction exhibited by boron-doped silicon, originally p-type but converted to n-type by the diffusion of lithium, was reversed by sufficiently high radiation doses. At room temperature, this change occurred some weeks after irradiation, whereas at 200°C, the change needed only an hour. The cause of the reversal in the type of conduction is obviously related to the disappearance of lithium donors, which, having been precipitated at defects, capture their “own” electrons and therefore destroy the overcompensation of the acceptor centers.

Crystals overcompensated with lithium can be used conveniently to study the energy spectrum of local centers in both halves of the forbidden band first by measuring the changes in the Hall effect, which yield information on the upper half of the forbidden band, and then, after reversal of the type of conduction, by investigating the levels lying closer to the valence band.

An unusually high stability of the defects, with which the $E_V + 0.28$ eV level is associated, was discovered

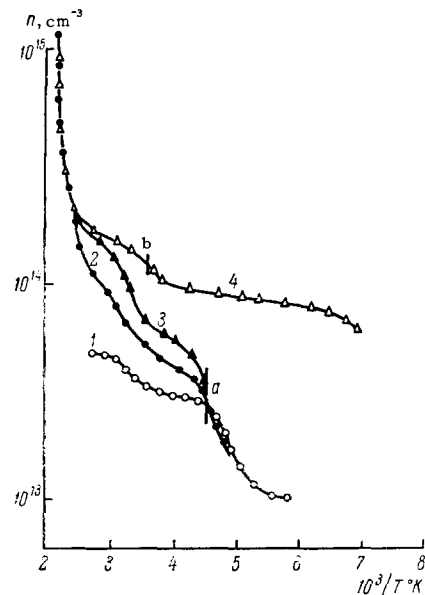


FIG. 5. Temperature dependence of the hole density in a silicon sample with lithium and residual boron. After irradiation, the conduction became p-type. Annealing for one hour at each of the following temperatures: 210°C; 340°C, 390°C, 450°C.

in a study of the high-temperature annealing of crystals which have again become p-type by the precipitation of lithium at radiation defects. Hill,^[17] Bemski and Augustyniak^[18] reported that near 450°C the radiation defects were annealed almost completely within several minutes. Figure 5 shows the temperature dependences of the hole density in one of the reversed-conduction samples after annealing at various temperatures for one hour. The curves rise along the ordinate axis as the hole density increases with annealing of the defects. The curve corresponding to the annealing at 450°C has retained the step “b” corresponding to the $E_V + 0.28$ eV level but the “a” step of the $E_V + 0.21$ eV level has disappeared.

The stability of the centers may be explained as follows: the complete annealing of radiation defects in silicon free of lithium represents the annihilation of a vacancy and an interstitial atom. If we assume that the defects responsible for the appearance of the $E_V + 0.28$ eV level include interstitial atoms (for example, complexes formed with oxygen atoms^[19]), such defects would disappear only with difficulty when vacancies are filled.

It is known that recombination levels may disappear when impurity centers interact with structural defects.^[20] One would expect to detect a similar effect on the basis of the phenomena observed after the irradiation of lithium-doped silicon. The short-circuit current (I_S) method was used to determine the lifetime; this current appears due to the diffusion of excess carriers produced in a crystal by electron excitation across a p-n junction. The method is convenient for obtaining recombination data directly during ir-

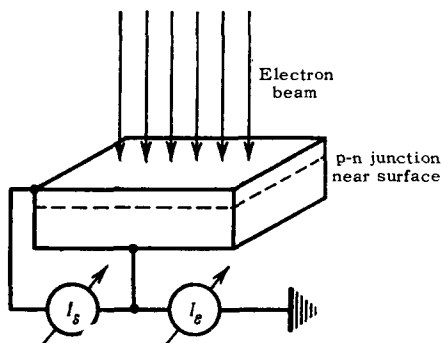


FIG. 6. Experimental arrangement for the determination of the recombination velocity of nonequilibrium carriers and of the threshold energy of radiation-defect formation in a semiconductor.

radiation with fast electrons (the current I_e), which are used both as the excitation source and as the means of generating defects. Silicon samples with surface barriers, prepared in the way usual for the purpose of charged-particle counting, were employed. Figure 6 illustrates the experimental arrangement. Figure 7 gives the change in the reciprocal of the square of I_s , which is proportional to the reciprocal of the nonequilibrium carrier lifetime, as a function of the integral 1 MeV electron flux for two samples with the same resistivity $\rho = 0.2$ ohm.cm and, consequently, the same position of the Fermi level. One sample was doped with lithium, the other with phosphorus. The oxygen content, according to the infrared absorption data, was practically the same for both samples and amounted to $(2-3) \times 10^{17}$ cm $^{-3}$. The tests were carried out at room temperature. Figure 7 shows that initially the lifetime decreases with increase of the electron flux in the same way for both samples but later the reduction in the lifetime in the lithium-doped sample slows down and then practically stops. The value of I_s^2 for the lithium-doped sample remains practically constant up to an electron flux of 4×10^{15} cm $^{-2}$, while for the phosphorus-doped sample it continues to decrease linearly.

We may assume that the process of the formation of recombination centers is limited by the diffusion of lithium, i.e., lithium interacts with the A-centers during irradiation.

On the other hand, the rate of generation of the dominant recombination centers may be limited also by the higher probability of the generation of centers of another type, for example, the centers with shallow levels referred to above.

4. THE NATURE OF RADIATION DEFECTS IN SINGLE CRYSTALS OF VERY PURE GERMANIUM AND OF GOLD-DOPED GERMANIUM

Beginning with the early work of K. Lark-Horovitz and his colleagues,^[23] germanium has been the classical material for the investigation of radiation defects

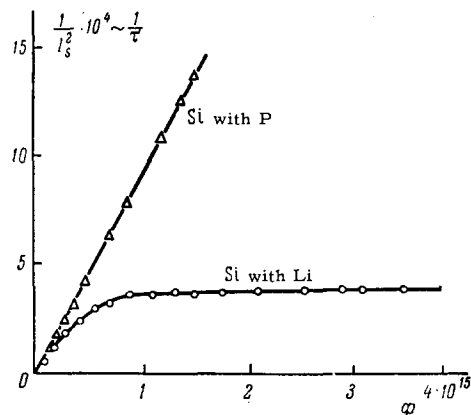


FIG. 7. Increase of the value of $1/I_s^2$, proportional to the volume recombination velocity of nonequilibrium carriers, in n-type silicon crystals doped with phosphorus (upper curve) or lithium (lower curve). The horizontal axis gives the integral flux of 1-MeV electrons.

and their influence on the electron processes in semiconductors. Several factors, discussed in detail at the Gatlinburg Conference in 1959,^[24] have made it, and still make it, difficult to identify the spectrum of local levels in irradiated germanium. One of these factors, which seems important to us, is the difficulty of observing the paramagnetic resonance.

Because of this, the studies of irradiated germanium are frequently directed toward the explanation of the nonequilibrium mechanisms of electron processes (photoconductivity, impurity breakdown, etc.) associated with radiation defects. These processes do not require, for their interpretation or for their practical application, the same extent of knowledge of the physical nature and origin of the defects which exists, for example, in the case of the A-centers in silicon. In keeping with the subject of this review, we shall not consider the results of such work but restrict ourselves to an analysis of the attempts to isolate the spectrum of the simplest defects and of the effects of their interaction with impurities.

I. P. Akimchenko, A. F. Plotnikov, and the present author^[25] used high-purity germanium single crystals containing residual impurities of groups III and V in amounts not exceeding 10^{12} cm $^{-3}$. The resistivity of these crystals was about 56 ohm.cm at room temperature. In the control tests, we used p-type samples doped with about 10^{15} cm $^{-3}$ of gold. The principal methods adopted were the measurement of the photoconductivity spectra and kinetics, and of the Hall emf. The germanium was irradiated with 1 MeV electrons at room temperature. After irradiation by a flux of the order of 10^{16} electrons/cm 2 at about 100°K, the equilibrium concentration of holes in p-type samples decreased to values of the order of 10^8 cm $^{-3}$. The photoconductivity was measured using the apparatus described in^[26].

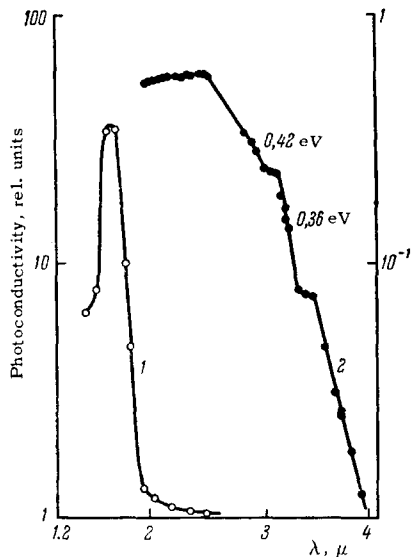


FIG. 8. Photoconductivity spectra of a single crystal of pure n-type germanium before (curve 1) and after (curve 2) irradiation with an integral flux of 2.2×10^{15} electrons/cm² (1 MeV). After irradiation, the sample became p-type. Temperature, 100°K.

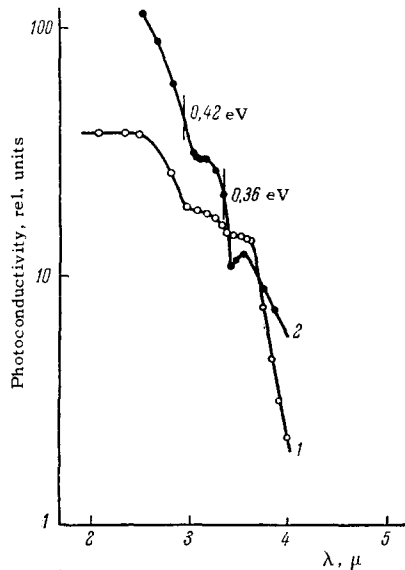


FIG. 9. Photoconductivity spectra of p-type germanium having high resistivity and low impurity concentration (about 10^{12} cm⁻³) before (curve 1) and after (curve 2) irradiation with a flux of 4×10^{15} electrons/cm². Electron energy, 1 MeV. Test temperature, 100°K.

Figure 8 shows the photoconductivity spectrum of the original n-type germanium (curve 1) and the spectrum of the same sample after irradiation with a flux of 2.2×10^{15} electrons/cm² (curve 2). The irradiation changed the type of electrical conduction to p-type. In the impurity region, the photoconductivity had steps near 2.8 and 3.8μ , which could be associated with electron transitions from the valence band to the $E_V + 0.36$ eV and $E_V + 0.42$ eV levels. The control tests, described in detail in [25], showed that the observed impurity spectrum was due to volume centers. In contrast to the spectra of n-type single crystals,

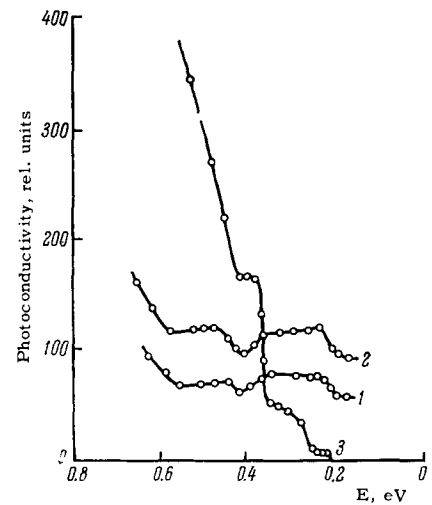


FIG. 10. Photoconductivity of a sample of gold-doped germanium, first unirradiated and then irradiated with various fluxes. 1) Before irradiation; 2) 8×10^{15} electrons/cm² flux; 3) 6×10^{16} electrons/cm² flux.

the $E_V + 0.36$ and $E_V + 0.42$ eV levels in pure p-type germanium were detected also in the original unirradiated material. Such a spectrum is shown in Fig. 9 (curve 1). Irradiation with a flux of 4×10^{15} electrons/cm² did not produce new levels in the investigated region of the spectrum but only increased the defect concentration. It seems natural to assume that the p-type conduction of the original crystals was due to intrinsic defects formed during crystal growth.

Curtis and Crawford, [27, 28] who investigated the annealing of defects in n-type germanium, suggested that the $E_V + 0.36$ eV level was due to vacancies. Akimchenko, Plotnikov, and the present author [25] suggested that the $E_V + 0.42$ eV level was due to interstitial atoms. Logan [29] showed that vacancies affect the electrical conductivity of rapidly quenched germanium samples, and suggested that interstitial atoms were captured by dislocations and did not appear as electrically active centers. If this is true then the $E_V + 0.42$ eV level should be absent in the photoconductivity spectrum of quenched germanium. Tests on the quenching of germanium in ethylene glycol from temperatures of 600–800°C showed that such samples did indeed have only the $E_V + 0.36$ eV level and not the $E_V + 0.42$ eV one. [25] Moreover, later experiments on dislocation-free single crystals of germanium [30] showed that the centers with the $E_V + 0.42$ eV level appeared in the samples heated to and quenched from 600–700°C, providing additional confirmation that this level was associated with interstitial atoms.

Experiments on the irradiation of germanium doped with gold confirm, in the author's opinion, the cited conclusions on the nature of centers with levels at $E_V + 0.36$ eV (vacancies) and $E_V + 0.42$ eV (interstitial atoms). It has been found that the presence of gold affects the rate of generation of these centers by radiation. Figure 10 shows the photoconductivity spectra of a gold-doped germanium sample, initially

unirradiated and then irradiated. Curve 1 represents the unirradiated sample; curve 2, the sample irradiated with a flux of 8×10^{15} electrons/cm². Both spectra are identical: irradiation with fluxes up to 1.5×10^{16} electrons/cm² does not change the spectra. They show the $E_V + 0.2$ eV level of gold. The minimum in the region of 0.4 eV is associated with the competing absorption by free holes.

Irradiation with sufficiently strong electron fluxes (6×10^{16} electrons/cm², curve 3) changes the form of the spectrum and gives rise to the levels at $E_V + 0.36$ eV and $E_V + 0.42$ eV. It has been suggested that in the case of electron fluxes producing vacancies in concentrations smaller than the concentration of gold atoms, the generated vacancies associate with gold atoms. Therefore, at room temperature, when the rate of vacancy migration is sufficiently high, we do not notice the formation of simple defects. At vacancy concentrations greater than the concentration of gold, some vacancies remain free and the $E_V + 0.36$ eV level is observed. If we assume that interstitial atoms of germanium do not interact as strongly with vacancies as do gold atoms, then the concentration of free interstitial atoms exceeds the concentration of free vacancies. Therefore, the relatively more pronounced appearance of the $E_V + 0.42$ eV level may be used as an additional argument in favor of the suggestion that this level is associated with interstitial atoms.

Analysis of the kinetics of the growth and decay of the photoconductivity signals associated with the $E_V + 0.36$ eV and $E_V + 0.42$ eV levels made it possible to determine the cross section for the capture of holes by these levels, which were found to be, at $T \approx 100^\circ\text{K}$:

$$E_V + 0.36 \text{ eV}, \quad \sigma_p \approx 1.5 \cdot 10^{-16} \text{ cm}^2;$$

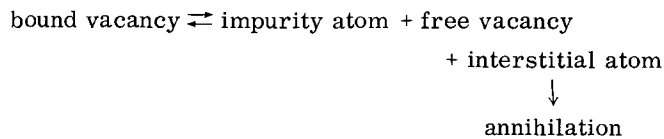
$$E_V + 0.42 \text{ eV}, \quad \sigma_p \approx 3 \cdot 10^{-17} \text{ cm}^2.$$

The efficiencies of generation of these levels by radiation were determined from the capture cross section data; within the experimental error, they were found to be identical for the two levels.

5. INTERACTION BETWEEN RADIATION DEFECTS AND IMPURITIES DURING ANNEALING

In 1959, Brown and Augustyniak^[31] showed that the annealing of radiation defects in germanium depended strongly on the type of conduction, the defect concentration and any additional illumination. The influence of oxygen and copper on the annealing of defects in silicon was noted by Bemski and Augustyniak.^[18] However, the theory of annealing—for example that given in the well-known work of Waite^[33]—does not allow for the influence of impurities. A. V. Spitsyn and L. S. Smirnov suggested^[34] that the impurity atoms may act as “trapping centers,” which slow down the process of recombination of vacancies and interstitial atoms, and they analyzed the annealing on

the basis of a kinetic model similar to that used frequently in the theory of luminescence. The annealing process, according to this model, is described as follows:



(it is assumed that vacancies are considerably more mobile than interstitial atoms).

Up to the time of appearance of this work of Spitsyn and Smirnov,^[34] no experiments had been carried out which could be used to verify this model unambiguously. However, the application of the model to, for example, the annealing of n-type germanium, studied in^[31,32], gives good agreement with experiment.

The most detailed investigation of the annealing of radiation defects produced by gamma rays in germanium containing Sb and As was carried out by Ishino, Nakazawa, and Hasiguti.^[35] The annealing was carried out between 310 and 560°K. The electron densities before irradiation (n_0), after irradiation (n_i), and after annealing (n), were determined at 90°K. As a measure of the degree of annealing, we used the fraction of the unannealed defects

$$f' \equiv \frac{n_0 - n}{n_0 - n_i} < 1. \quad (4)$$

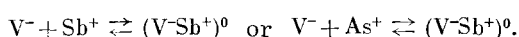
Taking into account the energy spectrum of defects in n-type germanium crystals^[36] and the temperature at which the measurements were carried out, we may conclude that the value of f' represents the relative change in the concentration of ionized acceptor levels of radiation defects. According to the James—Lark—Horovitz model,^[23] the difference $n_0 - n$ is proportional to the vacancy concentration. According to the Blount model^[37] both vacancies and interstitial atoms each have one acceptor and one donor level. Then the difference $n_0 - n$ is proportional to the total concentration of interstitial atoms (Int) and vacancies (V).

Using isochronous annealing (15 min), Ishino et al.^[35] discovered three different stages of the variation of f' .

Stage I—annealing in the 370°K region. The activation energy of 0.7–0.8 eV is close to the independently determined value of the activation energy for the interstitial diffusion of atoms. The kinetics of the annealing process is almost of the first order, as it should be for the interaction between closely spaced vacancies and interstitial atoms.^[33,38] However, Ishino et al.^[35] discovered that at this stage the behavior of germanium doped with antimony is quite different from that of arsenic-doped n-type germanium. In the latter case, the mobility in the impurity scattering region recovers almost completely at this annealing stage although the recovery of the carrier density just begins. Such behavior of the mobility may be associated with the

formation of neutral (at low temperature) IntAs^+ complexes. The negative charge of the interstitial atom at low temperatures follows from the Blount model. At the annealing temperature, when the Fermi level lies close to the middle of the forbidden band, the interstitial atom is, according to this model, neutral and we have the reactions $\text{Int}^0 + \text{As}^+ \rightleftharpoons \text{IntAs}^+$ and $\text{Int}^0 + \text{Sb}^+ \rightleftharpoons \text{IntSb}^+$. In the latter case, the equilibrium should shift toward higher concentration of free atoms at interstices (as indicated by the data of^[35]).

Stage II—annealing close to 430°K. The activation of energy of the process amounts to 1.2 eV, which corresponds approximately to the activation energy for the vacancy diffusion. In samples doped with antimony, the low-temperature mobility sometimes reaches higher values than those before irradiation, i.e., neutral complexes are formed at this stage as well, for example



This stage may be interpreted as the result of the diffusion of vacancies to interstitial atoms and donor atoms.

Stage III—annealing temperatures near 530°K. The activation energy is (2.20 ± 0.2) eV for germanium doped with arsenic and (2.5 ± 0.3) eV for germanium doped with antimony. The kinetics of the process is of the second order. This stage may be associated with the dissociation of (V^-As^+) and (V^-Sb^+) complexes, and the activation energy should correspond, approximately, to the sum of the binding energy of the complex and the activation energy for vacancy diffusion.^[34,38] We then find that the binding energy for the vacancy and the As atom is about 1 eV, and ≈ 1.3 eV for the vacancy and the Sb atom.

Using the association energy found by Ishino et al,^[35] we can calculate the number of jumps of an interstitial atom or a vacancy at a given temperature during a given annealing duration. * Since, at stages I and II, there is definite interaction between the components of Frenkel pairs and impurities, this number of jumps should have the same order of magnitude as the average distance l between a radiation defect and an impurity (taking into account the capture radius). † At stage I, when neutral interstitial atoms move to impurities, the interaction governing the capture is not of the Coulomb type. The capture radius is close to the lattice constant and the average distance which an interstitial atom has to travel to be captured by an impurity is large. Then the number of required jumps is found to be 10^2 – 10^3 times greater than the value calculated from the activation energy of 0.75 eV.

*The number of jumps is $n_j \approx 4\nu t \exp(-E/kT)$, where $\nu \approx 10^{13}$ sec⁻¹, E is the diffusion activation energy, T is the annealing temperature, and t is time.

† $l \approx (1/2)(N_d)^{-1/3} - r_t$, where N_d is the impurity concentration, and r_t is the capture radius.

Ishino et al assume that there is a barrier R for the annihilation of Frenkel pairs and that the observed experimental activation energy E may be represented as $E = E_m + R$, where E_m is the "intrinsic" activation energy for the diffusion of atoms.

Assuming that R is 0.15 eV and calculating the number of jumps from the diffusion activation energy $E_m = E - R$, Ishino et al removed the discrepancy.

It still remains incomprehensible how an interstitial atom "senses" at large distances the difference between the ionic radii of arsenic and antimony (1.19 Å for As^+ and 1.39 Å for Sb^+).

The completion of an annealing stage corresponds to the end of a given mechanism of Frenkel pair annihilation and the formation of complexes with impurities. Therefore, the completion of stage I should correspond to a situation when practically all the interstitial atoms are captured by impurities (at least, in arsenic-doped germanium). The next stage, II, cannot occur, as assumed by Ishino et al, after the dissociation of IntSb^+ or IntAs^+ complexes, since the reaction rate would then be determined by the rate of this dissociation and would be considerably different for the case of As and Sb. In fact, at stage II, we should have the process of vacancy diffusion to bound interstitial atoms and the annihilation of Frenkel pairs near impurity atoms. At the same time, there may be partial formation of the (vacancy + impurity atom) complexes, which dissociate at stage III. This interpretation is not final and needs to be checked.

Ishino et al did not study the influence of dislocations (they did not check the dislocation density). The possible simultaneous effect of dislocations and impurities on the processes of diffusion in semiconductors makes it difficult to interpret the defect annealing data. It is desirable to separate the effects of dislocations and impurities by investigating the annealing of material containing various amounts of impurities but known to be free of dislocations, and, conversely, a material with variable density of dislocations but a constant (low) impurity concentration.

Vitovskiĭ, Mashovets, and Ryvkin^[39] investigated the isothermal annealing of γ -radiation defects in samples containing 4×10^{13} and 2×10^{14} cm⁻³ of antimony at 120°C and 200°C. They investigated the reduction, during annealing, in the density of particular energy levels of radiation defects. The following observations were made:

a) The density of the $E_C - 0.2$ eV, $E_V + 0.27$ eV, and $E_V + 0.11$ eV levels decreased as a result of annealing; this decrease was represented by a single activation energy, equal to 1.3 ± 0.2 eV, which was identical with the activation energy of stage II annealing in the work of Ishino et al^[35] and, as previously mentioned, was only slightly greater than the activation energy for vacancy diffusion.

b) The main annealing mechanism was bipolar, i.e., there was a simultaneous reduction of the densities of

the donor ($E_C - 0.2$ eV or $E_V + 0.27$ eV) and acceptor ($E_V + 0.11$ eV) levels. In addition, there was monopolar annealing, usually of the donor levels but sometimes of the acceptor ones. Which of the defect levels was affected by the high-temperature monopolar annealing depended on whether there was strong monopolar annealing of the $E_C - 0.2$ eV level during irradiation. This annealing occurred partly in samples with various donor concentrations. However, the results of Cleland et al.^[40] force us to assume that the reason for the differences lay in the different dislocation densities, which were not measured by Vitovskii et al.

c) The $E_V + 0.27$ eV level changed into the $E_V + 0.22$ eV level at the early stages of the 200°C annealing of samples converted to p-type. When a sample recovered its n-type conduction after prolonged annealing it was found that the $E_C - 0.2$ eV level disappeared while a level at $E_C - 0.13$ eV appeared. The change of the position of this level was ascribed by Vitovskii et al to a change in the defect structure. It should be noted that, according to the Blount model, the $E_V + 0.27$ eV level is not associated with vacancies and is of acceptor type. From general considerations one would expect a reduction in the energy of the levels of a vacancy near a donor atom. Therefore, the $E_V + 0.22$ eV level may be interpreted as belonging to a vacancy located close to an impurity atom.

6. THE GENERATION OF RADIATION DEFECTS IN INTERMETALLIC SEMICONDUCTORS

In spite of the complexity of the processes of interaction of defects with impurities in germanium and silicon, the experiments involving the irradiation of semiconductors with mono-energetic electrons near the threshold of defect formation threw up new and interesting information on the primary process of atom displacement. We shall not deal with the "threshold" experiments carried out on Ge and Si, which are sufficiently well described in the literature,^[24,10] but we shall consider briefly the data obtained recently by Bäuerlein^[42] who investigated the generation of radiation defects in several intermetallic compounds. As in other work,^[21] the parameter which changed very greatly due to the appearance of defects was the volume recombination velocity for nonequilibrium carriers. The basic experimental arrangement has already been shown in Fig. 6. Plane-parallel samples of intermetallic compounds had p-n junctions, which were prepared by the diffusion of impurities and located just below (about 10μ) the flat surface. A monoenergetic electron beam, with which a "primary" current I_s was associated, penetrated these junctions. The ionization brought about by fast electrons produced nonequilibrium carriers near the p-n junctions. The nonequilibrium carrier density could be found by measuring the short-circuit current

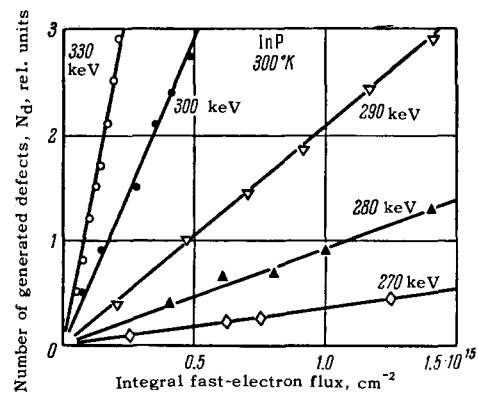


FIG. 11. Growth in the number of radiation defects, which influence the recombination velocity in InP, as a function of the radiation dose for various electron energies.

I_s between the p- and n-type regions.

If the energy of the fast electrons is greater than the threshold of defect formation, the ratio I_s/I_e should decrease with increase of the integral radiation dose. If the thickness of the sample and the electron penetration depth are sufficiently great compared with the carrier diffusion length, and if the defects are sufficiently stable at the annealing temperature, the number (N_d) of recombination-center defects produced is proportional to the corresponding rise in the quantity $(I_s/I_e)^{-2}$:

$$N_d \sim \Delta \left(\frac{I_s}{I_e} \right)^{-2}. \quad (5)$$

Examples of typical experimental data are the dependences shown in Fig. 11 for the compound InP. An interesting property, discovered by Bäuerlein in an analysis of the dependence of the ratio N_d/N_e (where N_e is the integral electron dose) on the electron energy, is the existence of not one but two threshold energies for each of the binary semiconductors. Each of these thresholds should naturally be associated with the process of a displacement from lattice sites of one of the two components of the compound. In the case of atoms differing greatly in their mass (such as, for example, P and In), there seems to be no doubt about the conclusion that the lower threshold, at 110 keV, corresponds to the displacement of phosphorus atoms from their sites, while the threshold near 270 keV is associated with indium atoms.

In the case of a head-on collision between an electron of energy E and an atom, the latter acquires the energy

$$T_m = 2 \frac{m}{M} E \left(\frac{E}{mc^2} + 2 \right) \quad (6)$$

or

$$T_m = \frac{560.8}{A} \epsilon (\epsilon + 2) \text{ [eV]}, \quad (7)$$

where A is the atomic weight, $\epsilon = mc^2$, m is the electron mass, M is the atomic mass, and c is the velocity

difference between the energies necessary for the "knock-out" generation of defects and for the displacement of atoms by thermal excitation, the table includes some self-diffusion energies.

The appearance of more or less stable recombination centers as a result of irradiation determines the operational stability and the service life of semiconducting devices, in particular particle counters and electron-excited masers.^[46]

The problem of the stability of radiation defects in semiconducting compounds requires further study for which crystals with reproducible properties are needed. Preliminary data obtained on InSb and GaAs show that the majority of the generated defects anneal at room temperature.^[45]

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