Helium-Temperature Annealing of Electron-Irradiated n-Type Germanium†

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n-type germanium (4×10^{14} Sb/cm^3) has been irradiated with 1.1-MeV electrons at 5 °K. The defects produced have been studied by measuring the voltage-dependent capacitance of a metal-germanium junction formed at the surface of a germanium sample. These measurements were made at 10 °K and directly gave the charge density near the surface of the sample. The production and recovery of defects seen near the surface is the same as seen in bulk experiments. A 0.5-MeV electron beam was used to cause radiation annealing of the defects at 5 °K. The fraction recovered during radiation annealing is directly proportional to $t^{1/2}$. A model based on diffusion-limited-recovery theory is used to explain these results. This model is also used to discuss the results of previous experiments. The temperature dependence of the observed recovery at 5 °K gave a defect migration energy of 0.0044 ± 0.008 eV.

I. INTRODUCTION

The purpose of this experiment is to study the defect production and recovery found in lightly doped n-type germanium after electron irradiation at low temperatures.

Electron-irradiation-damage experiments have been performed on germanium at low temperatures since 1959. The majority of these experiments have been studies of the most prominent feature of irradiation behavior in n-type Ge, the annealing stage at 65 °K.[1–3] For light irradiations at low temperatures (10 °K or less) and energies (less than 1 MeV) almost 100% recovery in conductivity is seen in the 65 °K peak.[3] This nearly complete recovery along with the observation of a stored-energy release of about 5 eV per defect during the recovery,[4] indicates that the annealing is the result of interstitial-vacancy annihilation.

Attempts to devise a model to describe damage recovery in n-type Ge have been only partly successful. MacKay and Klontz have introduced both a close-pair model[1] and a model based on long-range motion of the interstitial,[5] but because of the peculiar kinetics of the 65 °K annealing stage and other complex phenomena observed in n-type Ge, neither model has been completely satisfactory.

It has been observed that the defects introduced by a 1-MeV electron irradiation of n-type Ge at low temperatures can be almost completely annealed at these temperatures by continuing the irradiation with electrons of less than 0.5-MeV energy.[1–3] This process, radiation annealing, and a similar observation that broad-band light of less than the band-gap energy will also cause almost complete annealing at 4.2 °K[6] show that the annealing seen in n-type Ge is dependent on the charge state of the defect. The present experiment attempts to gain new information about defect production and annealing by studying the recovery during radiation annealing.

Defects that change the population of carriers by introducing levels into the band gap can be very easily detected by electrical measurements. Direct-current conductivity measurements can be made on degenerate Ge ($n>2\times10^{17}$/cm^3) down to 4.2 °K. In nondegenerate or lightly doped n-type Ge, conduction electrons are frozen out at 4.2 °K. In fact, useful dc conductivity measurements cannot be made below 30 °K. Calcott has described a high-field conductivity measurement that, with the use of short infrequent pulses, allows radiation damage in nondegenerate Ge to be studied at 4.2 °K.[3]

In the present experiment a differential-capacitance measurement is made on a metal-germanium junction at 10 °K. This technique has the advantage of allowing an accurate measurement of the density and distribution of charged defects and of allowing measurements to be made in a very small region near the surface of the sample. Comparison of production and recovery near the surface with that in the bulk can be used to give information about the long-range migration of defects.

II. DIFFERENTIAL-CAPACITANCE-MEASUREMENT THEORY

The differential-capacitance technique has been widely used to study impurity atom distribution in semiconductors. This technique requires the use of a reverse-biased abrupt asymmetrical p-n junction, or a similar structure such as a metal-semiconductor junction, located so that a space-charge layer is created in the volume of the semiconductor being studied. The conditions under which the charge density of impurity atoms and charged defects in the space-charge layer, or depletion region, can be obtained from a measurement of the variation of the junction capacitance with applied bias voltage have been discussed by various investigators.[7–12]

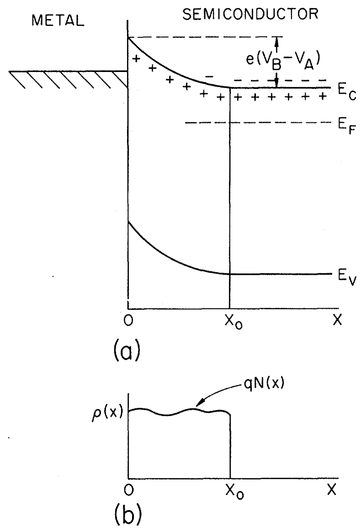

FIG. 1. (a) Potential diagram of a metal-semiconductor contact under reverse bias ($v_A < 0$). (b) Charge density in the semiconductor as assumed in the approximate model used in Sec. II. The value of $N(x)$ is an arbitrary junction of position.

From Shockley's depletion-layer theory,[13] the case of an abrupt junction, as shown in Fig. 1, gives

$$x_0 = \kappa\epsilon_0 / C \,, \tag{1a}$$

$$N(x_0) = \frac{2}{\kappa\epsilon_0 q} \frac{dV}{d(1/C^2)} \,, \tag{1b}$$

where x_0 is the width of the depletion region, κ is the dielectric constant, ϵ_0 is the permittivity of free space, q is the electron charge, C is the barrier capacitance per unit area, V is the total voltage drop across the junction, and $N(x_0)$ is the net fixed charge density at x_0. These equations give the net charge density as a function of distance into the sample away from the metal-semiconductor junction from measurement of the ac capacitance of the junction as a function of applied bias voltage. The circuit which represents the metal and semiconductor is shown in Fig. 2(a). G is a voltage dependent conductance[14] associated with the depletion layer. Equivalent circuits are shown in Figs. 2(b) and 2(c).

Kennedy, Murley, and Kleinfelder[11] have pointed out that differential-capacitance measurements actually establish the majority-carrier distribution in a semiconductor, not necessarily the fixed-charge density. However, Eqs. (1a) and (1b) are quantitatively correct when applied to a semiconductor in which charge neutrality is not locally disturbed. A method for measuring the impurity atom distribution when local charge neutrality has been disturbed has been reported by Kennedy.

The differential-capacitance method has been previously applied to the study of radiation damage in Ge.[15] That experiment used p-n junction structures which were measured at 77 °K. Metal-semiconductor devices were used in the present experiment so that the region of the crystal under study would not have to be subjected to the doping and diffusion steps required to make a p-n junction and so that a region near an external surface could be studied. In the present experiment measurements were made at 10 °K. Useful measurements could not be made at temperatures lower than 10 °K because of the rapid increase in the bulk resistivity at low temperatures.

III. EXPERIMENTAL PROCEDURE

The samples for this experiment were made from a single-crystal ingot of antimony-doped germanium which was purchased from Eagle-Picher Industries. This boat-grown crystal had a resistivity of 3 Ω cm and an etch-pit density of less than $1500/\text{cm}^2$. This resistivity indicates a nominal antimony atom density of $5\times10^{14}/\text{cm}^3$. Slices made from this ingot were polished and chemically etched in CP-4 to a thickness of about 200 μ. Silver was evaporated onto the freshly etched slice in an oil-free high-vacuum system. An array of 1-mm² silver dots formed the metal-semiconductor junctions on which subsequent measurements were made. A large dot (about 1 cm in diam) was evaporated onto the back of each slice to provide a low-resistance contact. Contact is made to the 1-mm² silver dots on the front of the sample by attaching 0.0025-in. copper wires with a small drop of silver paint. Care is taken to be sure that the silver paint

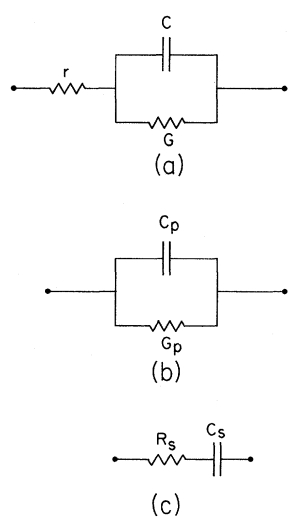

FIG. 2. (a) Actual circuit for a metal-semiconductor junction. (b) Parallel equivalent circuit. (c) Series equivalent circuit.

does not contact the Ge surface, only the silver dot. Contact is made to the large back dot in a similar fashion.

The experiments were performed in a 5-liter 1 liquid-helium cryostat purchased from Superior Air Products Co. The sample was cooled by helium exchange gas in a tail piece similar to that described by Whitehouse *et al.*[16]

The capacitance was measured on a General Radio type 1615-A capacitance bridge which was able to measure the capacitances found in this experiment (about 100 pF) to ±0.01 pF.

The accuracy of the capacitance and voltage measurements allow a measurement of the change in charge density in the depletion region to be made to $\pm 1\times10^{12}/cm^3$ in a sample with a background doping of about $10^{14}/cm^3$.

The temperature of the sample was measured by measuring the resistance of a carbon resistor in thermal contact with it. The resistance of the carbon resistor had been measured at 4.2 and 77 °K to provide the calibration for a resistance-versus-temperature curve which is used for the intermediate temperatures. A 10-μA current is passed through the carbon resistor and the voltage drop across it is measured with a Leeds and Northrup type K-3 potentiometer.

All samples were irradiated by the Materials Research Laboratory Van de Graaff electron accelerator. The defect production irradiations were done at 1.1 MeV with currents of 2.5×10^{-9} A/cm^2 at the sample. If the sample was to be radiation annealed, it was heated to a predetermined temperature (5–10 °K), and irradiated with a 5×10^{-9}-A/cm^2 beam of 0.5-MeV electrons for a carefully measured length of time. The beam was then shut off and capacitance-versus-voltage measurements were made and the process repeated.

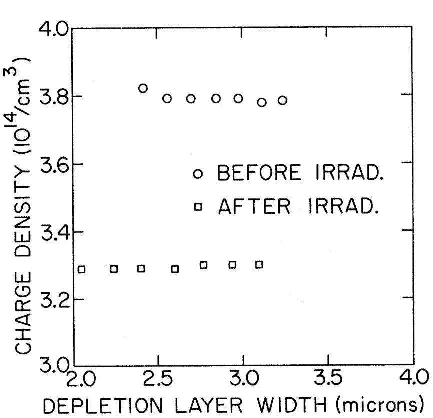

FIG. 3. The charge density $N(x)$ as a function of distance before and after irradiation, measured at 10 °K using capacitance-vs-voltage data before and after irradiation with 1.1-MeV electrons.

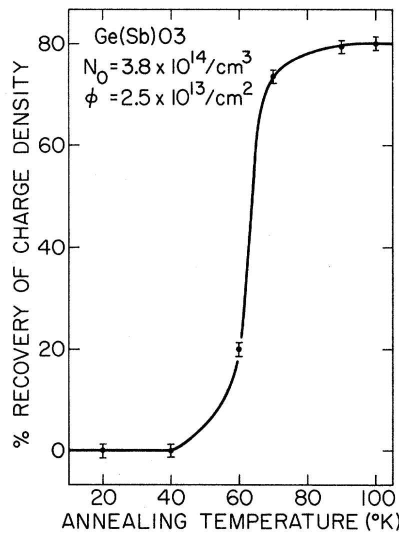

FIG. 4. Isochronal anneal of n-type G, where N_0 is the charge density before irradiation, and ϕ is the 1.1-MeV electron flux; 7-min anneals.

IV. EXPERIMENTAL RESULTS

All of the data to be presented here was taken on n-type Ge with a doping of $\sim 4\times10^{14}$ Sb/cm^3. All of the measurements were made at 10 °K. The first group of results, as shown in Figs. 3–6, were attempts to look for deviations from previously reported results by studying recovery near the surface, and by changing irradiation intensities and temperatures.

Ge(Sb)03 was irradiated at 10 °K. The charge distribution before and after 2.5×10^{13} electron/cm^2 is shown in Fig. 3. The annealing of Gb(Sb)03 was studied in a manner similar to that reported by Calcott and MacKay.[3] The sample was quickly heated to the annealing temperature, held there

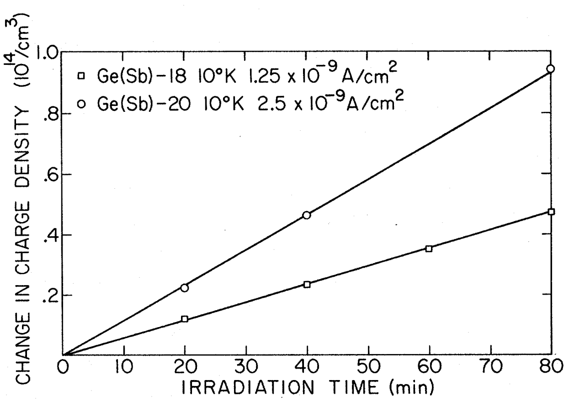

FIG. 5. Defect production as a function of time for two beam currents.

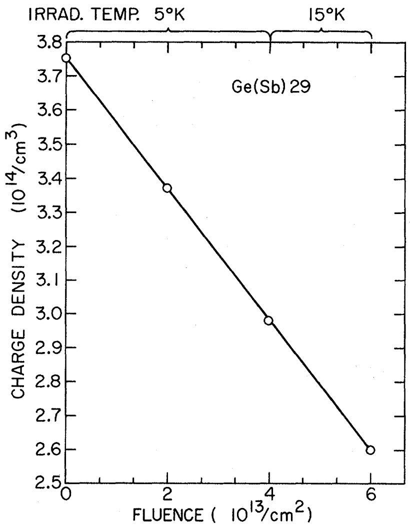

FIG. 6. Defect production at two irradiation temperatures.

for 7 min, then quickly cooled down to 10 °K where a measurement was taken and then the process repeated. As reported by Calcott and MacKay,[3] essentially the only recovery seen in this region is (80 ± 2)% in one stage centered at 65 °K. The results are shown in Fig. 4.

Ge(Sb)16 and Ge(Sb)18 were used in attempts to see if the irradiation temperature affected the percent recovered in a long anneal (15 min) at 70 °K. Ge(Sb)16 (6 °K) recovered (77 ± 2)%, Ge(Sb)18 (10 °K) recovered (77 ± 2)%.

Ge(Sb)18 and Ge(Sb)20, as shown in Fig. 5, and Ge(Sb)29, as shown in Fig. 6, showed that the change in charge density (i.e., the number of defects) produced per incident electron/cm^2 was the same (1.9 ± 0.1/cm) for two beam densities (2.5×10^{-9} and 1.25×10^{-9} A/cm^2) and three irradiation temperatures (5, 10, and 15 °K).

The second group of results presented (Fig. 7) shows the data taken during radiation annealing at different temperatures on samples irradiated with 2.5×10^{13} electron/cm^2 at 1.1 MeV. It has been observed that irradiating a damaged sample with an electron beam of 0.5 MeV or less will cause nearly complete recovery at low temperatures of the damage ordinarily recoverable at 65 °K.[1–3] While radiation annealing has been previously thought to be due to localized heating by the beam, Arimura and MacKay[6] have shown that the same process can be observed merely by shining light on the sample at 4.5 °K. If this were only an electronic effect, without actual defect recovery, heating the sample to 10 °K as is done in this experiment would cause these defects to again assume their equilibrium charge state, and no recovery would be seen.

Figure 7 shows the result of plotting the fraction recovered ϕ as a function of $t^{1/2}$; the significance of this will be discussed later.

The main results of the present experiments were the following: (a) Production rates and the amount of thermal annealing through the 65 °K peak were essentially the same as reported in bulk experiments.[3] (b) Defect production/cm^3 per electron/cm^2, 1.9 ± 0.1/cm, was independent of irradiation temperature and beam intensity. (c) The present recovery in the 65 °K peak [(77 ± 2)%] was independent of the irradiation temperature. (d) The defects produced with a 1.1-MeV beam could be annealed with 0.5-MeV electrons. The fraction recovered was proportional to $t^{1/2}$, where t is the 0.5-MeV irradiation time. This proportionality was also a function of temperature (at ~ 5 °K). (e) The amount of damage introduced or recovered does not depend on the distance from the surface of the sample.

V. DISCUSSION

A. Correlated-Recovery Model

Zizine[17] has recently reported a careful study of the kinetics of the 65 °K annealing peak. He shows that the recovery can be described as a diffusion-controlled recombination of correlated pairs. Correlated recovery is the annihilation of an interstitial with its own vacancy after making a number of jumps, in close-pair recovery the intersitial only makes one jump.[18] The motion of the interstitial in correlated recovery is controlled by diffusion.

The time and temperature dependence of this type of recovery have been described in several papers.[19–21] The following assumptions are used: (a) The interstitial migrates freely in three dimensions. (b) Interstitial-vacancy annihilation occurs

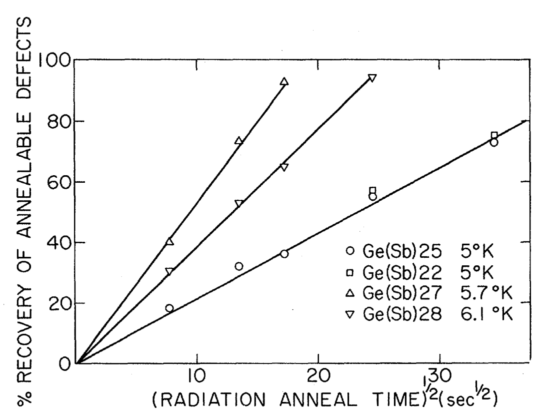

FIG. 7. Recovery as a function of $t^{1/2}$ for various samples. Radiation annealing with constant beam current at the temperature shown.

when an interstitial comes within a critical radius r_0 of the vacancy. (c) The initial distribution of interstitials is described by some function. In this case a modified Gaussian distribution function is used. (d) All Frenkel pairs are isolated and uniformly distributed.

Let $P(\vec{r}, t)\,dv$ be the probability that an interstitial is in the volume element dv at a distance $\vec{r}$ from its vacancy at time t. This probability is assumed to obey the diffusion equation

$$\frac{\partial P(\vec{r}, t)}{\partial t} = D\nabla^2 P(\vec{r}, t)\,, \tag{2}$$

where D is the diffusion constant and ∇^2 is the Laplacian. The previous assumptions are equivalent to the following boundary conditions for Eq. (2):

$$P(r \le r_0, t) = 0\,, \tag{3a}$$

$$P(r, t=0) = Ae^{-(r/\lambda r_0)^2}\,, \quad r > r_0 \tag{3b}$$

where A is a normalization constant and λ is a parameter to be determined from the fitting experimental data. The probability that a vacancy-interstitial pair is separated a distance r at a time $t=0$ is given by

$$\rho(r)dr = Ae^{-(r/\lambda r_0)^2}\, 4\pi r^2\, dr \tag{4}$$

and A is evaluated by requiring

$$\int_{r_0}^{\infty} \rho(r)\, dr = 1\,. \tag{5}$$

The rate equation is obtained by letting the number of defects which disappear per unit time be equal to the flux of interstitials through a sphere of radius r_0 around a particular vacancy.

If n is the concentration of interstitials and if at $t=0$, $n=n_0$, then the fraction ϕ recovered is $\phi = (n_0 - n)/n_0$. Solution of the rate equation then gives the fraction recovered as a function of time and of the diffusion constant, for $(Dt)^{1/2} \ll \lambda r_0$,

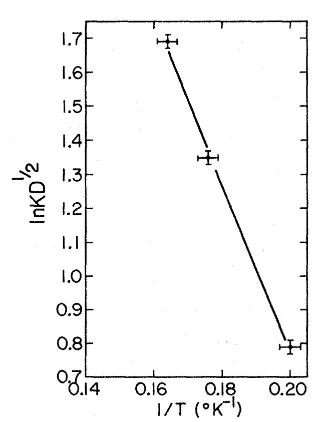

FIG. 8. Recovery rate, from Fig. 7, as a function of temperature.

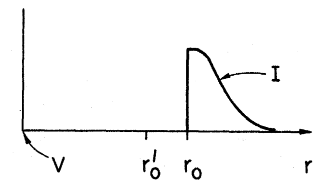

FIG. 9. Proposed model for the distribution of interstitials around their vacancies. No interstitials for $r > r_0$ (r'_0 is the critical radius in thermal equilibrium at 65° K).

$$\phi = B[4(Dt)^{1/2}/\pi^{1/2}\lambda^2 r_0]\,, \tag{6a}$$

where

$$B = [1 + \tfrac{1}{2}(\pi^{1/2}\lambda)\, e^{1/\lambda^2}\, \mathrm{erfc}(1/\lambda)]^{-1}\,, \tag{6b}$$

where $\mathrm{erfc}(x)$ is the complimentary error function evaluated at x. The above can be expressed as

$$\phi = K(Dt)^{1/2}\,, \tag{7a}$$

where

$$K = -4B/\pi^{1/2}\lambda^2 r_0\,. \tag{7b}$$

Therefore, the assumptions given above lead to the result that the fraction of defects annealed is proportional to $t^{1/2}$ if they are undergoing correlated recovery. This dependence is observed in the present experiment.

The slopes of the curves shown in Fig. 7 give $KD^{1/2}$ for each temperature over this range, the K is temperature independent and the change in slope with temperature seen in Fig. 7 gives the temperature dependence of D. Assuming that D has the form

$$D = D_0\, e^{-E_m/kT} \tag{8}$$

it follows from Eqs. (7a) and (8) that

$$\ln(\text{slope}) = \text{const} - E_m/2kT\,. \tag{9}$$

This can be solved graphically, as shown in Fig. 8, to give $E = 0.0044 \pm 0.0008$ eV for defect motion during radiation annealing.

As mentioned above, Zizine has found that the 65 °K annealing stage can be explained by correlated recovery.[17] He has shown that the asymptotic behavior of this type of recovery, in the region $(Dt)^{1/2} \gg \lambda r_0$, will result in $\phi\, \alpha\, 1/(Dt)^{1/2}$, where ϕ is the fraction recovered. Analyzing his results on this basis, Zizine finds that the activation energy for the 65 °K peak is $E = 0.15 \pm 0.01$ eV. As $(Dt)^{1/2}$ is a measure of the distance a defect moves before annihilation, and λr_0 is a measure of the average interstitial-vacancy separation, it might be expected that these quantities would be the same for the 5 °K radiation annealing and the 65 °K thermal annealing if the same defects are involved in both stages. While the 65 °K recovery takes place with the defects in their equilibrium charge states, the low-temperature recovery is apparently the result of altering the defect charge states with light or radiation. With the altered charge states, the interstitial-vacancy annihilation may be assisted by Coulomb attraction. Therefore, the critical radius for annihilation, r_0, would be larger and the distance of free diffusion smaller in the low-temperature case.

On the basis of the above discussion the following model is proposed for the production and recovery of the defects that recover at 65 °K in n-type Ge:

Interstitial-vacancy pairs are formed during irradiation, with the distance between these defects varying due to the distribution in the energy transferred to the interstitials. Interstitials that stop at a distance less than r_0 from the vacancy will be annihilated during the irradiation. After irradiation the damage will consist of vacancies with their interstitials in a distribution at $r > r_0$, as shown in Fig. 9. During the radiation annealing at 5 °K these interstitials undergo diffusion-limited recovery with an apparent migration energy of 0.0044 eV.

At 65 °K, the interstitials, presumably in their equilibrium charge states, are able to move with a migration energy of 0.15 eV. As pointed out above, the critical radius for annihilation in this case, r_0', is expected to be smaller than in the radiation annealing case, where Coulomb attraction is assumed to create a larger radius of annihilation. The distribution shown in Fig. 9, with r_0' as the annealing radius, will show the $1/t^{1/2}$ dependence at long times, as observed by Zizine.[17] However, a complete calculation, for all times, can be made for the distribution in Fig. 9. Approximating the interstitial distribution at r_0 with a δ function,

$$P(r, t=0) = \delta(\beta r_0' - r)/4\pi(\beta r_0') , \tag{10}$$

where

$$\beta r_0' = r_0 , \tag{11}$$

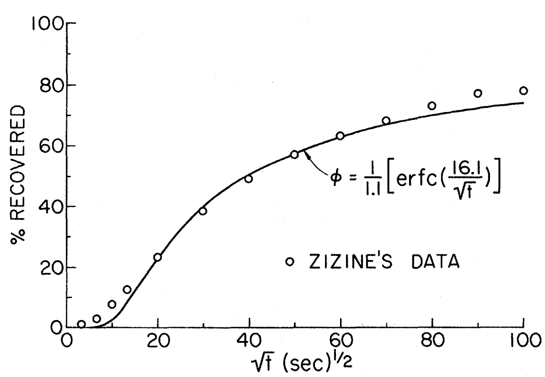

FIG. 10. Zizine's data (Ref. 17) compared with calculations that assume a δ-function distribution of interstitials at r_0, as shown in Fig. 9.

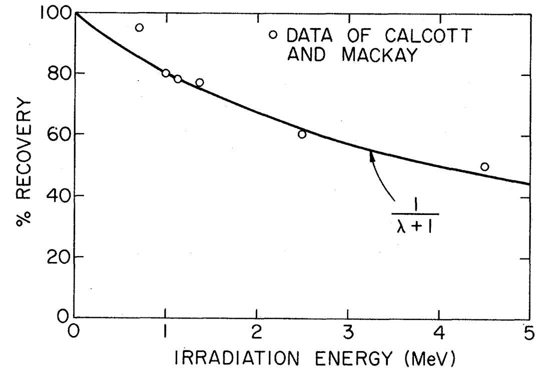

FIG. 11. Dependence of the recovery in the 65 °K annealing state on the energy of the bombarding electrons. The data are from Callcott and MacKay with the curve given by $1/1+\lambda$, where $\lambda = 0.25E$ (MeV).

results in

$$\phi = (1/\beta)\{\mathrm{erfc}[r_0'(\beta - 1)/2(Dt)^{1/2}]\} . \tag{12}$$

This has been plotted, as shown in Fig. 10, and compared with Zizine's data. Zizine's results have been questioned because of the delayed annealing seen at short times. This type of annealing result is now seen to be a characteristic of having a region near r_0' that is depleted of interstitials. Therefore, the more detailed correlated-recovery model proposed here is able to explain Zizine's observations.

As no uncorrelated recovery is seen, the interstitials that escape correlated recovery with their own vacancy are eventually trapped, probably by impurities, and do not participate in these recovery processes.

An estimate of r_0 can be made by calculating the distance at which the Coulomb attraction is large enough to surmount the activation barrier. Therefore, we have

$$F\tfrac{1}{2}a_0 = (e^2/\kappa r_0^2)\tfrac{1}{2}a_0 = 0.0044 \text{ eV}, \tag{13}$$

where a_0 is the distance between adjacent equilibrium defect positions (2.44 Å for Ge), κ is the dielectric constant, and e is the electronic charge. Equation (29) gives $r_0 = 15.9$ Å. This value for r_0, along with the data from this experiment, and

$$D = D_0 e^{-E_m/kT} \tag{14}$$

allow D_0 to be calculated with the result being $D_0 = 10^{-15}$ cm^2/sec. To fit Zizine's 65 °K annealing data, the D_0 required is of the order of 10^{-9} cm^2/sec. However, assuming

$$D = 4\nu a_0^2 , \tag{15}$$

where ν is the atomic vibration frequency ($\sim 10^{13}$/sec) and a_0 is the distance between lattice positions (2.44 Å), gives $D_0 = 0.024$ cm^2/sec.

These anomalous values of D_0 suggest that this defect migration is different from that normally observed. One possibility is that other processes are required for migration, such as defect ionization, and that these alter the effective D_0. Further work will be required to decide what meaning should be attached to the unusual values observed for D_0.

The correlated-recovery model can also by used to explain the dependence of the fraction recovered at 65 °K on the energy of the incident electrons, as was observed by Calcott and MacKay.[3] This model predicts that as the energy of the incident electrons increases, the separation between an interstitial and its vacancy becomes greater (i.e., the distribution function spreads). To be specific, λ is expected to depend on the energy of the incoming electrons. The above theory predicts that the total number of defects to undergo correlated recovery is given by $\phi = 1/(\lambda+1)$, so that increasing the electron energy implies an increase in λ causing the fraction recovered to decrease. The recovery seen in Ge as a function of electron energy by Calcott and MacKay[3] can be explained with this model by letting $\lambda = 0.25E$, where E is the incident electron energy in MeV. See Fig. 11 for these results. Simpson and Chaplin[21] have studied the dependence of one electron energy for irradiation damage of aluminum and have found λ proportional to E.

B. Conclusion

Cahn[22] has calculated that 1-MeV electrons incident on Ge or Si will produce about 4.0 defects/cm^3 per electron/cm^2 if the displacement energy T_d is 15 eV. As the displacement energy increases to 30 eV, the defect production drops to about 1.0 defects/cm^3 per electron/cm^2. As T_d for Ge is in the range 15–20 eV, and T_d for Si is about the same, larger defect production rates than have been observed would be expected, except for n-type Ge at low temperatures. Watkins[23] has reported 0.03 defects/cm^3 per electron/cm^2 in p-type Si irradiated at 5 °K, with defect production about a factor of 10 lower in n-type Si. p-type Ge irradiated at 10 °K shows less than 3×10^{-4} defects/cm^3 per electron/cm^2.[24] In n-type Ge irradiated with 1.6-MeV electrons at 77 °K there are 0.65 electrons removed/cm^3 per electron/cm^2. Only in n-type Ge, irradiated with 1-MeV electrons at 20 °K or less, does the result, 2.0 electrons removed/cm^3 per electron/cm^2,[3] agree with theoretical predictions.

Radiation-damage behavior in n-type Ge for irradiations above and below 77 °K, and comparison of these results with observations in Si lead to some general conclusions. The dominant process occurring during irradiation and n- and p-type Si and p-type Ge at low temperatures, and in n-type Ge above 77 °K is interstitial-vacancy recombination. The defects remaining after irradiation under these conditions appear to be due to the escape of a small percentage of interstitials. These interstitials are apparently able to move easily through the lattice until they are trapped, or interchanged with substitutional impurity atoms. The efficiency of the interstitial-vacancy recombination varies from essentially 100% in n-type Si to about 80% in n-type Ge irradiated at 77 °K.

In n-type Ge irradiated at low temperatures, a large fraction of the created primary defects appear to remain after irradiation. This is probably related to the fact that these defects are stable to 65 °K in their equilibrium charge states. The recovery of these defects is a diffusion-limited correlated recovery with some interstitials escaping to initiate the process seen in the other materials (i.e., n-type Ge irradiated at 77 °K, and p-type Si). Long-range migration does take place in n-type Ge, but it does not appear to be part of the primary recovery process. The various ionization effects seen in n-type Ge are apparently due to the presence of both the vacancy and the interstitial with their multiple-charge states.

Future experiments should attempt to check the validity of Watkins's results, particularly the impurity–Si-interstitial interchange. In germanium considerable further work will be required to determine the charge states of both the vacancies and the interstitials. In addition, information is needed concerning migration energies of interstitials and of vacancies in various charge states. Attempts should also be made to understand the remarkable values of D_0 observed in the present experiments.

VI. SUMMARY

n-type Ge (4×10^{14} Sb/cm^3) has been irradiated with 1.1-MeV electrons at low temperatures (5–15 °K). The defects produced were studied by using a differential-capacitance measurement on a metal-Ge junction formed at the surface of the irradiated Ge crystal. This measurement gave the charge density in the Ge directly, and allowed measurements to be made on a small region of the semiconductor 1–3 μ from the metal-semiconductor junction. All measurements were made at 10 °K, where this method is much more sensitive than bulk conductivity measurements.

The important results were that the production and recovery seen near the surface are essentially the same as seen for bulk experiments, and that the fraction of defects recovered during radiation annealing at 5 °K is proportional to $t^{1/2}$. As this $t^{1/2}$ dependence is predicted by diffusion-limited correlated-recovery theory, a model was proposed in which the interstitials are assumed to be found in a distribution around their own vacancies, and that these defects anneal out by correlated recovery.

The temperature dependence of the observed recovery at ~ 5 °K gave an apparent migration energy of 0.004 eV.

A discussion of the general features of defect production and recovery of Ge and of possible energy level models was given. The relationship of the present results to the work of Zizine,[17] and the extension of this model to explain Calcott and MacKay's recovery-versus-energy data[3] were also discussed.

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Need for a Nonlocal Correlation Potential in Silicon

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An attempt is made to fit cyclotron masses and principal energy gaps for silicon using a Heine-Abarenkov–type determination of the core-valence interaction fitted to the atomic spectra of Si^{3+}. The valence-valence exchange and correlation potential is approximated by a local potential. The masses and gaps are found to obey a "$\vec{k}\cdot\vec{p}$-type" product relation under variations of the local potential. The theoretical product is 10–25% smaller in absolute value than the experimental product. We conclude that a local approximation to exchange and correlation is inadequate for silicon. If the masses are fitted the gaps are in error by 0.5–0.7 eV. We suggest that screened Hartree-Fock exchange may provide the nonlocality required to overcome these fitting difficulties.

I. INTRODUCTION AND CONCLUSIONS

A basic problem in all band calculations is the choice of potential. Most so-called *a priori* calculations use the Slater "$\rho^{1/3}$" approximation[1] to exchange and correlation. Variations on the $\rho^{1/3}$ method have been suggested such as the use of $\nabla\rho$ corrections and the empirical adjustment of the prefactor multiplying $\rho^{1/3}$.[2] All these methods are characterized by being "local" potentials, i.e., the potential operator may be taken as $V(r)$ rather than the more general $V(r, r')$. The Hartree-Fock approximation involves a nonlocal potential. However, the nonlocality is strongly reduced by screening[3] so that quantitative estimates of the importance of nonlocality have not been made.

In the empirical pseudopotential method[4] the effective potential is assumed to be local and so rapidly convergent in momentum space that it can be adequately represented in silicon by the three lowest Fourier coefficients $\tilde{V}_{111}$, $\tilde{V}_{220}$, and $\tilde{V}_{311}$, all others being taken to be zero. Empirical values for these coefficients in germanium and silicon were first obtained by Brust.[5]