tron velocities, of 0.85. In view of the fact that there is a small density of electrons in states with a negative velocity with respect to the field, this indicates that the distribution is in fact highly anisotropic and nearly linear.

The calculated generation rate for InSb is in very good agreement with the values measured by McGroddy and Nathan.[14] For a given generation rate the electric field of the calculated generation rate seems to be roughly 15% below the experimental field although the slopes of the curves are in excellent agreement. The difference in the fields could be accounted for by saying that the effective electron velocity is not v but really $v\cos\theta$, since this would require a slight increase in the field to obtain the same theoretical generation rate. This would also be consistent with the drift-velocity results. In view of the lack of a precise value for ϵ^* and in view of the many necessary approximations which must be made in any theory of pair generation, perfect agreement should, perhaps, not be expected.

For InAs there is at present no data of the generation rate although Steele and Tosima[16] have observed a large increase in the carrier concentration at approximately 1000 V/cm. This is in excellent agreement with what we would expect from our calculations of the generation rate although the translation of a generation rate into a breakdown field is only a guess unless one has detailed information about the recombination mechanisms. The drift velocity obtained by Steele and Tosima was, however, in considerable disagreement with our predictions, having a maximum value of only 1.3×10^7 cm/sec. More recent measurements[17] of the drift velocity have yielded values of $2\text{–}3\times10^7$ cm/sec, but low-temperature measurements on suitably pure InAs have not yet been made.

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[16] M. C. Steele and S. Tosima, Japan. J. Appl. Phys. **2**, 381 (1963). This presents room-temperature data; however, there is no significant change in the breakdown field down to 77°K according to M. C. Steele (private communication).

[17] J. W. Allen, M. Shyam, and G. L. Pearson, Appl. Phys. Letters **9**, 39 (1966); J. S. Harris (private communication).

PHYSICAL REVIEW VOLUME 167, NUMBER 3 15 MARCH 1968

Bombardment-Produced Defects in *p*-Type Germanium at Low Temperatures*

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(Received 14 August 1967)

Lattice defects produced in nondegenerate (1–10 Ω cm) *p*-type germanium at 10°K by 1.0-MeV electrons cannot be detected electrically immediately following bombardment. Illumination by light having energy less than the band gap reveals the defects in the form of ionized donors. During ionization, the carrier concentration decreases as the sum of two exponentials, with time constants in the ratio ≈6 to 1. Subsequent thermal-annealing investigations show two recovery stages in the temperature range 40 to 70°K. These stages appear to be intimately related to the time constants for decay during illumination, with the low-temperature recovery associated with the fast component and the high-temperature recovery with the slow component. Both stages of recovery are independent of the type of impurity. Regardless of the extent of illumination, the electrical conductivity and the carrier concentration have essentially the same values they had prior to bombardment. When illuminated sufficiently long to ionize all the defects, the ionized donors become extremely susceptible to annihilation when the temperature is increased, and the situation after heating to 70°K represents true annealing. Illumination for shorter times results in some un-ionized defects which do not anneal upon heating to 70°K. Isochronal heating to 150°K then causes a transformation of most of the unannealed defects into a configuration which the authors call a "two-state defect," the same defect observed following irradiation at 77°K. The transformed defects break up at about 200°K. Along with the higher-temperature effects, some impurity-dependent recovery stages are noted. A model to partially account for the results is briefly discussed.

I. INTRODUCTION

ONE of the most interesting results to come from electron-irradiation experiments on germanium at low temperatures is the striking difference in behavior between *n*-type and *p*-type Ge. At 77°K, defects are introduced into both types by 1-MeV electrons, but the introduction rate for *p*-type material is about a fourth or a fifth of that for *n*-type material. For 10°K bombardments with 1.1-MeV electrons, Klontz and MacKay[1] were not able to measure any change in the electrical properties of degenerate *p*-type Ge due to electron bombardment, nor did they observe any changes due to annealing of defects on heating the

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* Work supported by contract with the U. S. Atomic Energy Commission.

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[1] E. E. Klontz and J. W. MacKay, J. Appl. Phys. **30**, 1269 (1959).

sample to 100°K following irradiation. Contrasted with this, degenerate *n*-type Ge showed both damage and annealing under these conditions.

Extending the work on degenerate *p*-type Ge to higher energies, Whitehouse[2] found that damage is observed as a result of 4.5-MeV bombardment at 10°K. However, the introduction rate for the defects was found to be about a factor of 25 smaller than for similarly treated *n*-type samples. Whitehouse further found that when light of energy less than the band gap illuminated the sample after irradiation, a substantial number of previously unseen defects were revealed, observed by a decrease in the electrical conductivity. Upon heating, a process which tended to restore the conductivity was observed between 30 and 90°K, and another which had the reverse effect was seen between 70 and 110°K. Observation of both of these annealing processes was found to be related to prior illumination. Throughout these experiments, Whitehouse saw no measurable changes in the Hall coefficient.

In the present work the problem of electron damage in *p*-type Ge by 1-MeV electrons at 10°K is reexamined. The Hall coefficient and the electrical conductivity are used to study the defects. Referencing the measurements to a temperature near 30°K allowed nondegenerate material to be used, avoiding the difficulties previously encountered with sensitivity and absence of measurable change in the Hall coefficient when degenerate material was used. All the thermally induced modifications of the defects detected by changes in the electrical properties have occurred at temperatures higher than 30°K, and the use of electronic circuitry to stabilize the temperature and to increase the speed of the measurements has made measurements of the electrical properties near 30°K feasible.

II. EXPERIMENTAL

The liquid-helium cryostat has been described elsewhere,[1] but the tailpiece and wiring have been recently modified to accommodate two samples simultaneously. The specimens were placed on a copper post, one in front and to the side of the other, so that both samples would have unobstructed exposure to the electron beam. Windows of 1-mil Mylar in the sample and exchange gas compartments allowed the electrons and light to enter. A Globar provided a source of infrared light which was focused by a concave mirror, and entered the system through a thick intrinsic germanium filter. A disk containing an aperture and a plane mirror was arranged so that it could be rotated either to allow electrons to strike the sample when the aperture was properly positioned, or to reflect infrared light onto the samples when the mirror was rotated into position.

The samples were cut from vacuum-grown single crystals. X-ray orientation permitted the crystals to be cut so that a (110) plane was bombarded. The samples were ground and then etched in CP4, so that their final dimensions were approximately 10×1×0.1 mm. Just before mounting, the samples were rinsed in HF. Probes for the electrical measurements consisted of 1-mil wires attached to the samples with indium. The 1-mil wires were then soldered to 3-mil wires attached to a plug, the mate of which was in the cryostat tailpiece.

An automatic measuring system was designed by the authors and is to be described at some length in a planned publication, so only a functional description will be given here. The term "automatic measuring system" is here applied to a collection of circuits and devices which provide the means for automatically measuring and recording the voltages and currents necessary for the determination of the temperature and of the values of the Hall coefficient and electrical conductivity for two samples. The voltages are taken from a Cimron 7500A digital voltmeter, a five-significant-figure automatic potentiometric device with full-scale ranges from 9.9999 mV to 999.99 V with 0.01% relative accuracy. A Hewlitt-Packard 561B digital printer is used to record the readings of the digital voltmeter. Using this system a measurement of the temperature, electrical conductivity and Hall coefficient for two samples can be made with 0.1% relative accuracy in 80 sec.

The samples were irradiated with electrons from a pulsed microwave linear accelerator with energy variable from 0.3 to 1.5 MeV. The bombardment energy for the damaging irradiations was 1.0 MeV. Irradiations were performed using an approximately constant flux of 2×10^{11} electrons/cm^2 sec, and the sample temperature was observed to be between 8 and 10°K during the bombardment. All samples were preirradiated, at an energy below the threshold for damage (350 keV), to saturate the surface states.[3]

III. METHODS OF ANALYSIS

For nondegenerate *p*-type Ge doped with group III impurities, changes in the carrier concentration as the donor concentration or the acceptor concentration are changed are described by

$$p+N_d=N_a/[1+(4p/N_v)e^{\epsilon/kT}], \qquad (1)$$

where p is the carrier concentration, N_a is the acceptor concentration, N_d is the donor concentration, k is Boltzmann's constant, T is the absolute temperature, and $N_v=2(2\pi m^*kT/h^2)^{3/2}$. The values of ϵ, the acceptor activation energy, are known from optical measurements.[4] The values of N_a and N_d can be obtained from measurements of p versus T by regarding Eq. (1) as an equation in two unknowns, N_a and N_d. A collection

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[2] J. E. Whitehouse, Phys. Rev. **143**, 520 (1966).

[3] J. M. Kortright, Ph.D. thesis, Purdue University, 1963 (unpublished).

[4] R. L. Jones and P. Fisher, J. Phys. Chem. Solids **26**, 1125 (1965).

of measured points (p_i,T_i) is arranged in the order of descending temperature. Then all reasonably spaced pairs of points [e.g., (p_j,T_j) and (p_m,T_m), $j>m+3$] are used to calculate values of N_a and N_d. The values of these quantities will vary for each pair of points chosen, because of experimental error, so the arithmetic average is taken. The average deviation is then a measure of the accuracy of the determination. A FORTRAN IV program was used to accomplish this chore.

It can be shown from Eq. (1) that $|dp/dN_d|$ increases as the temperature decreases. Thus, by measuring changes in carrier concentration in nondegenerate material at temperatures below the exhaustion temperature of the acceptor levels, an enhanced sensitivity to defects is obtained.

The carrier concentration was obtained from the Hall coefficient by assuming that $r=\mu_H/\mu=1$. Brown[5] has reported that this assumption is a good one for p-type Ge if $\mu_H H>10^7$ G cm^2/V sec. For the samples used in the experiments to be described here, this criterion was satisfied for temperatures of about 30°K and below. Furthermore, curves derived by fitting p versus T data obtained from measurements at temperatures of 30°K and below to Eq. (1), also fitted the p versus T measurements up to about 60°K. Hence, for these experiments, r will be taken as unity below 60°K for the samples used.

Methods of analysis of the annealing curves have been described by several authors[6,7]; hence, the description of these methods need not be repeated here.

IV. EXPERIMENTAL RESULTS

A. Changes During Irradiation and Illumination

In agreement with the results of Klontz and MacKay, very little damage was observed in nondegenerate ($\approx 10^{15}$ holes/cm^3) p-type Ge during bombardment. The removal rate was found to be less than 3×10^{-4} (holes/cm^3)/(electrons/cm^2). This is about a factor of 30 smaller than the upper limit given by Klontz and MacKay. This factor can be attributed to the increased sensitivity of the measurements on nondegenerate material. The mobility shows a very small increase during irradiation (about 0.6% for 3×10^{15} electrons/cm^2).

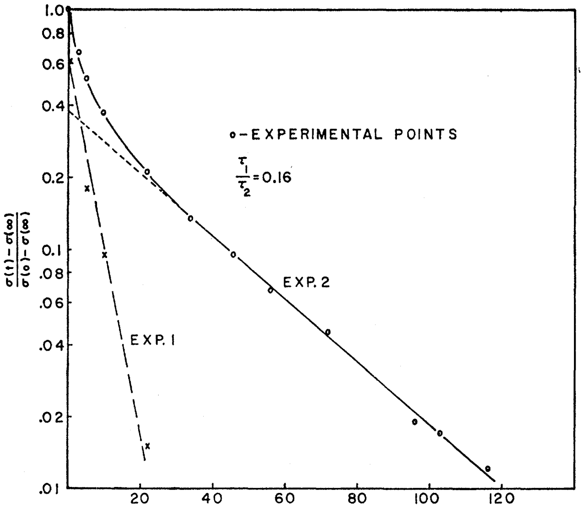

FIG. 1. Conductivity decay during infrared illumination at 5°K following 1.0-MeV electron irradiation at 10°K. Points are measured at a reference temperature of 33°K. The curve containing the experimental points is the sum of two exponentials.

Following irradiation, if the samples are illuminated at 5°K with light of energy less than the band gap, the carrier concentration and the electrical conductivity are observed to decay. Using the method outlined in Sec. III, we found the defects revealed by the light to be ionized donors. In Fig. 1, the manner in which the fractional change in the conductivity varies with the time of illumination is illustrated. This decay can be resolved into two independent exponential decays where the ratio of the long-time constant to the short-time constant is about 6 to 1. The short-time constant accounts for about 60% of the total change. Using the same designations as Whitehouse, the short-time constant will be called Exp. 1 and the long-time constant Exp. 2. For all experiments using illumination, the illumination is at 5°K and is of energy less than the band gap.

B. Annealing Results

The defects revealed by illumination have been observed to undergo several transformations as the samples are annealed. Significant annealing has been observed in four temperature ranges: 40 to 70°K; 100 to 150°K; 200 to 270°K; and 380 to 420°K. The 200–270°K and the 380–420°K stages have been studied by Brown, Augustyniak, and Waite[8] for material irradiated at 77°K. We have studied the first three annealing stages; these are discussed separately below.

After annealing samples, irradiated at 10°K, to room temperature, the defects which remain appear mostly as donors which are stable at temperatures below about 380°K. These remaining defects were not observed to have any effect on the formation of new defects at low temperatures or on the annealing of the new defects. Hence, after annealing to room temperature, the samples could be recooled and used for further experimentation.

Recovery for 40–70°K. After the defects have been revealed by the illumination, isochronal anneals to 80°K, referenced to 33°K, yield curves like those shown

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[5] D. M. Brown, Ph.D. thesis, Purdue University, 1961, p. 38 (unpublished).

[6] T. M. Flanagan, Ph.D. thesis, Purdue University, 1966 (unpublished).

[7] A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon and Breach Science Publishers, Inc., New York, 1963), Chaps. 2 and 3.

[8] W. L. Brown, W. M. Augustyniak, and T. R. Waite, J. Appl. Phys. **30**, 1258 (1959).

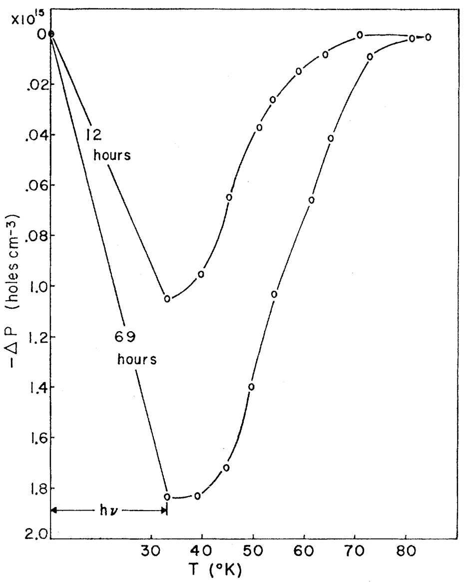

FIG. 2. Isochronal annealing of the carrier concentration following infrared illumination at 5°K of bombarded p-type Ge. Initial concentration was about 5×10^{14} cm^{-3} and the sample received 3×10^{15} electrons/cm^2 prior to each of the two periods of illumination. Measurements were referenced at 33°K.

in Fig. 2. Except for the duration of the illumination, the two experiments shown in Fig. 2 were performed under identical conditions. It is seen that the carrier concentration completely recovers in the temperature range 40–70°K. A complete recovery in the electrical conductivity is also observed.

To verify that the light-induced change and the 40–70°K recovery result only when the samples are exposed to damaging radiation, the samples were irradiated with 2.6×10^{15} electrons/cm^2 at 350 keV. The specimens were then illuminated for 20 h and annealed. The changes in the carrier concentration and electrical conductivity during the entire experiment were less than 0.1%; i.e., about equal to the precision of the measurements.

Once the defects have been ionized by illumination, their behavior is very susceptible to their charge state.

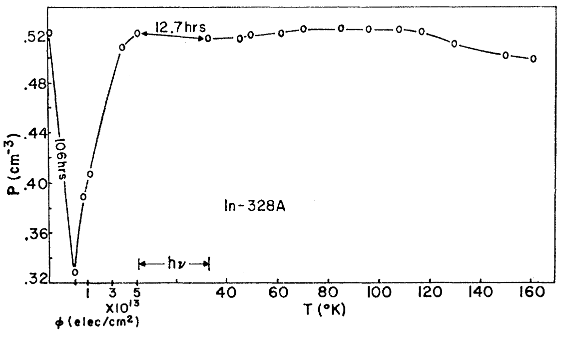

FIG. 3. Radiation annealing of ionized defects. Following 5×10^{13} electrons/cm^2 irradiation, the defects have disappeared and do not reappear with an additional illumination of 12.7 h.

The results of illumination followed by ionizing radiation are shown in Fig. 3. The specimens were bombarded at 10°K and then exposed to illumination until both Exp. 1 and Exp. 2 were complete. After further irradiation with 5×10^{13} electrons/cm^2 (1 MeV) at 10°K, complete recovery is observed. The changes resulting from further illumination and annealing are about what one would expect from 5×10^{13} electrons/cm^2 at 1 MeV. Hence, it appears that irradiation can produce the same effects as the 40–70°K recovery.

Analyses of the isochronal anneal curves like those shown in Fig. 2 suggested that the 40–70°K recovery consists of two overlapping stages. To investigate this possibility, annealing runs at a constant warming rate were performed.

Before the results of such annealing runs could be interpreted, the cause of the carrier-concentration change observed during the 40–70°K recovery had to be determined. To determine how the quantities N_a and N_d were affected by the 40–70°K recovery, we carried out analyses of measurements of the carrier concentration versus temperature which were made before and after the 40–70°K recovery. These analyses showed that, within the accuracy of the determinations (greater than 2%), only the donor concentration changes during this recovery. Thus, dN_d/dT gives the rate at which defects are disappearing as the sample is warmed.

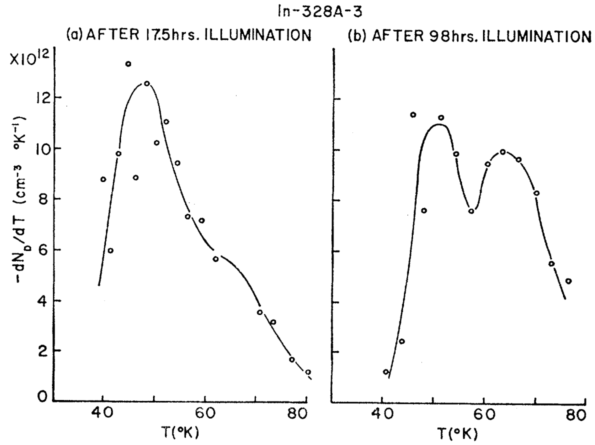

FIG. 4. Results of annealing using a constant rate of heating method following illumination. After 17.5 h of illumination the high-temperature stage of annealing is just beginning to become resolved. The growth of this stage with 98 h of illumination suggests the long-time constant exponential is associated with the high-temperature annealing stage.

From computer-analyzed measurements of the carrier concentration and of the temperature as the specimens were warmed, dN_d/dT was determined. The results of two such runs are shown in Fig. 4, where dN_d/dT is plotted against temperature. Although the values of dN_d/dT inherently contain a large degree of uncertainty, these curves suggest that there are two stages of annealing in the 40–70°K region, one centered near 50°K and the other around 65°K. The characteristic temperature for each stage will depend on the rate of warming, thus in Fig. 4(a) a slower warming rate produces slightly lower temperatures for each stage.

Analyses of either the constant-warming curves or of the isochronal annealing can establish activation energies and frequency factors for the associated annealing. An accurate determination of these values requires a precision which we are reluctant to claim owing to first-order assumptions and to experimental difficulties in either maintaining an extremely uniform rate of warming together with measurement of Hall coefficients to better than 0.10% for the constant warming, or producing rise times in approaching a temperature which are short compared to the time at that temperature for isochronal annealing. Following the treatment of Damask and Dienes,[7] it can be shown that the value of the activation energy for the constant warming run is given by

$$E = 2.45(kT_m^2/\Delta T_0), \tag{2}$$

where T_m is the temperature of the maximum in the $-dN/dT$ versus T curve and ΔT_0 is the width of the curve at

$$\tfrac{1}{2}(-dN/dT)_{\max}.$$

Using this analysis a value of $E \sim 0.05$ eV is obtained for the 65°K stage and $E \sim 0.04$ eV for the 50°K peak. Whether these two values do indeed differ is problematical since the uncertainty in each is greater than 0.01 eV.

For comparison, the isochronal annealing curve is plotted in Fig. 5. A break in the curve in the vicinity of 50–60°K again suggests two processes are involved with activation energies about the same as for the constant warming analysis. Frequency factors for the two types of annealing are not in very good agreement, but are of the order of 200 to 4000 sec^{-1}. Such low values may be accounted for by an analysis similar to Whitehouse's[2] where the density of sinks are $\sim 10^{12}$/cm^3. Whether there is a single activation energy and two different frequency factors such as might be obtained in a capture by two traps having different capture cross sections, or whether two different processes are involved requires more experimental evidence than we can provide at this time.

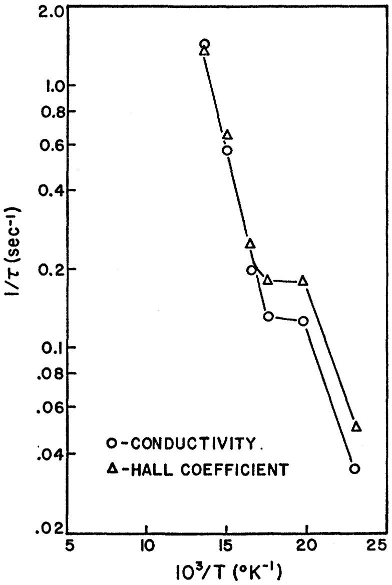

FIG. 5. Analysis of isochronal annealing data for the 40–70°K recovery. The ordinate plotted is $1/t \log 1/f_i$, where f_i is the fraction annealed at the temperature point indicated and t is the time (420 sec) maintained at that temperature.

In Fig. 4 the ratio of the area for the 50°K stage to that for the 65°K stage is approximately 3:1 for 17.5 h of illumination and about 1:1 for 98 h of illumination. Since Exp. 1 is essentially complete after 17.5 h of illumination, this suggests that the growth of the 65°K annealing stage is strongly dependent on Exp. 2. On this basis the 50°K annealing stage could be associated with Exp. 1 and the 65°K peak with Exp. 2. Confirmation of this association is obtained from an examination of Fig. 2. After 12 h of illumination, there is 70% recovery in the carrier concentration by the time a temperature of 50°K is reached; after 69 h of illumination only 40% recovers up to a temperature of 50°K, although the change in the carrier concentration from 35–50°K is the same for both. Again, the magnitude of the recovery above 50°K apparently grows with the degree of completion of Exp. 2. A third experiment provides further evidence of the relation between the 65°K annealing stage and Exp. 2. These results are shown in Fig. 6. After irradiation and 20 h of illumination (Sec. A), Exp. 1 is about 95% complete and Exp. 2 is about 40% complete. The specimens were then annealed to 55°K (Sec. B). Illumination was resumed at 5°K (Sec. C), and the further decay of the carrier concentration is found to be pure Exp. 2. Then the specimens were isochronally annealed over the entire 40 to 70°K temperature range a second time (Sec. D).

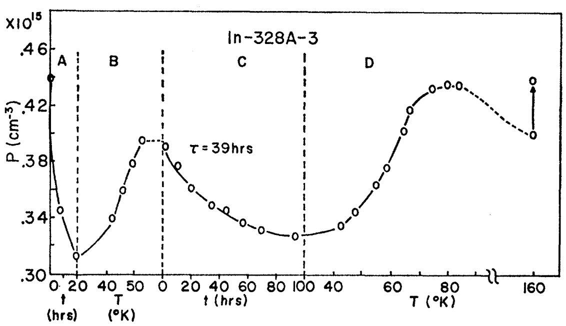

FIG. 6. Combination illumination and isochronal annealing experiment for correlation of annealing stages with the two exponential decays due to illumination. Sections A and C represent decays due to illumination. Sections B and D are isochronal anneals.

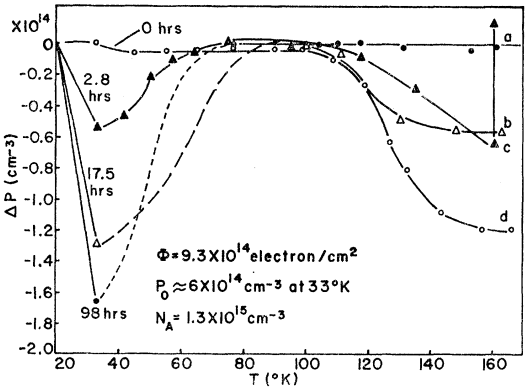

FIG. 7. Association of the 100–150°K transformation with the extent of illumination following bombardment. After each curve the sample was annealed at room temperature, bombarded at 10°K with 9.3×10^{14} electrons/cm^2, illuminated for the period of time shown, and measured during isochronal annealing to about 160°K. The vertical line for curve c indicates the presence of two-state defects.

Only 14% of the total carrier-concentration recovery occurred below 55°K for the second annealing, confirming the above association.

The 40 to 70°K recovery was observed in specimens doped with boron, aluminum, gallium, indium, and thallium, and no impurity-dependent differences could be detected.

100–150°K Transformation. Although following heat treatment to 80°K the samples are found to have completely recovered their prebombardment values of the conductivity and carrier concentration, the specimens have in general not returned to their prebombardment condition. If annealing is continued above 100°K, a decrease in the carrier concentration and conductivity is observed. Defined by the temperatures between which it is observed, this decrease will be called the 100–150°K transformation.

That the size of the decrease in carrier concentration and conductivity during the 100–150°K transformation depends on the duration of the illumination is shown by the isochronal anneals, based at 33°K, for various times of illumination, as illustrated in Fig. 7. After 98 h of illumination, Exp. 1 and Exp. 2 are both complete (cf. Fig. 1); and no 100–150°K transformation is observed (curve a). For 17.5 h of illumination Exp. 1 is essentially complete, but Exp. 2 is less than half complete. For this experiment some of the 100–150°K transformation is observed (curve b). For 2.8 h of illumination, Exp. 1 is less than half complete, Exp. 2 has hardly started, and a larger 100–150°K transformation appears. The largest such transformation is seen when the specimens are annealed immediately after bombardment with no illumination (curve d). A careful study of curves similar to Fig. 7 in the temperature region from 100–150°K shows that for samples doped with boron or aluminum small peaks arise, while for samples doped with thallium, indium, and gallium there are no peaks. This impurity-dependent behavior will be discussed in connection with impurity effects.

If the temperature of the bombarded specimen is rapidly raised and held at some constant value between 100 and 150°K, both the conductivity and carrier-concentration decay. Figure 8, taken at 126°K, shows that the fractional change of the carrier concentration decreases exponentially with time indicating a first-order process. Both isothermal and isochronal annealing experiments give an activation energy of 0.10 eV and an effective frequency of 10 sec^{-1} for this transformation.

C. Two-State Defect

Following the 100–150°K transformation, the defects have assumed a configuration which we call the "two-state defect." This is the configuration which is present after irradiating similar material at 77°K. To assist the interpretation of the results which follow, a brief summary of the known properties of this defect is given.

The two-state defect is reasonably stable below 80°K in either of two states. From mobility data, Callcott and MacKay[9] have assigned charges of (0) and (+1*e*) to these states. The defect behaves somewhat like a long-lived minority carrier (electron) trap. It can be reversibly cycled between either of these two charge states.[8,10] A short burst of ionizing radiation, e.g. fast electrons or x rays, puts the defect in the (0) state. Vertical lines near 160°K in Fig. 7 show the results of putting electrons on the defects by a burst of 350 keV electrons. The (+) state can be obtained by either

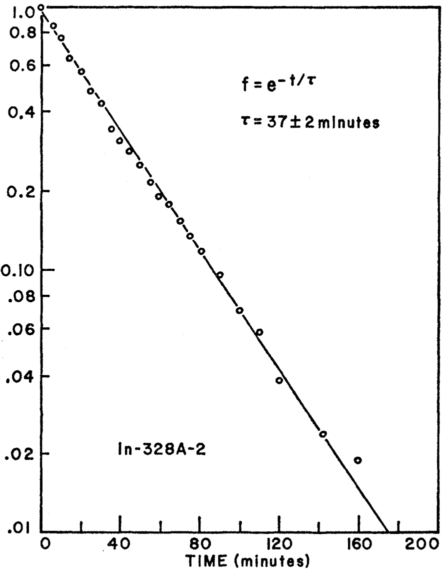

FIG. 8. Analysis of an isothermal anneal at 126°K for the 100–150°K transformation. Both isochronal and isothermal anneals indicate an activation energy of 0.10 eV associated with the transformation.

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[9] T. A. Callcott and J. W. MacKay, Phys. Rev. **161**, 698 (1967).

[10] T. A. Callcott, M.S. thesis, Purdue University, 1963 (unpublished).

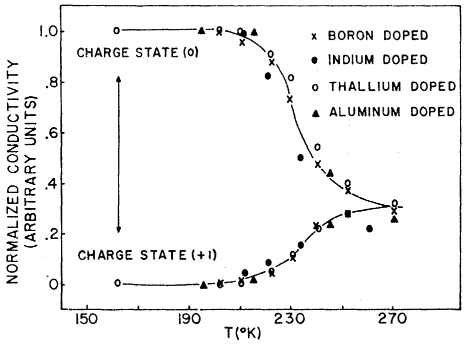

FIG. 9. Normalized isochronal annealing above 150°K shows the breakup of the two-state defect. Reference temperature for these experiments was 77°K. Samples are cycled between the two charge states using a short burst of ionizing radiation for the (0) state or by heating at 150°K for a few minutes for the (+1) state.

illuminating the sample with light of energy less than the band gap or by heating the sample to about 150°K for about 10 min. The rate at which the change of state is induced by the light is quite small.[9,10] The capture cross section of the defect for holes is less than 10^{-27} cm^2 in the (0) state.[8] This is too small for an uncharged defect; too small even for a defect with a double plus charge.[9] Hence, the defect cannot be a simple electron trap, and for lack of a more precise term we will call it the "two-state defect."

The thermal activation of the electrons from the two-state defects does not obey a simple kinetic scheme, although the excitation is governed by a single activation energy of 0.2 eV. These results, for samples irradiated at 10°K and then annealed to 150°K, agree with those of Callcott and MacKay[9] for specimens irradiated at 77°K. The activation energy was found to be independent of impurity type within the accuracy of the determinations (about 10%).

The two-state defect breaks up near 200°K. Figure 9 shows normalized isochronal annealing data, based at 77°K, for four samples. Since the defects lose their electrons before the specimens reach the annealing temperature, this plot represents annealing in the (+) state. After 5 min at each temperature, the samples are cooled and measured at 77°K. This gives a point on the lower curve of Fig. 9. A short burst of 350-keV electrons then puts electrons on those two-state defects which have not annealed, and another measurement is taken. This measurement gives a point on the upper curve of Fig. 9. Hence, the vertical distance between the two curves is proportional to the number of two-state defects remaining after each annealing temperature. Note that aluminum-, boron-, indium-, and thallium-doped material all follow the same curves. This breakup is found to follow first-order kinetics,[8] with an activation energy of 0.40 eV and an effective frequency of 5×10^6 sec^{-1}.

The breakup of two-state defects is the only modification of defects in p-type Ge which we have found to definitely remove acceptor levels of some of the chemical impurities. Using carrier statistics described earlier (Sec. III), analyses of measurements of carrier concentration versus temperature were made before and after each transformation of the defects. Although small changes in the number of acceptors at the chemical acceptor energy were noticed following the lower-temperature transformation, all such changes were less than or about equal to the accuracy of the determination (about 3% in most cases). Following the breakup of the two-state defect, typical results of such analyses are shown in Fig. 10, where the computer fits to Eq. (1) are shown by the solid lines. After the breakup of 2×10^{14} cm^{-3} two-state defects, about 9×10^{13} cm^{-3} acceptors have been removed from 0.01 eV, the chemical acceptor energy. This change amounts to about 10% of the total number of acceptors. As another example, after ten bombardments with a total dose of 1.3×10^{16} electrons/cm^2 at 10°K and anneals to room temperature, the acceptor concentration in one specimen went from 0.60×10^{15} cm^{-3} to 0.45×10^{15} cm^{-3}. The computer fit is to an equation representing the filling of a single level. Thus, the deviation of the experimental points for curve b at the high-temperature end ($10^3/T<15$) may be due to the ionization of the altered acceptor states. The Fermi level is about 0.04 eV above the valence band there. However, deviations of this sort could also arise if the ratio of the Hall mobility to the drift mobility were to become greater than unity.

D. Impurity-Dependent Effects

The shape of the annealing curve for the breakup of the two-state defect in gallium-doped material is anomalous, as shown by Fig. 11. The solid line con-

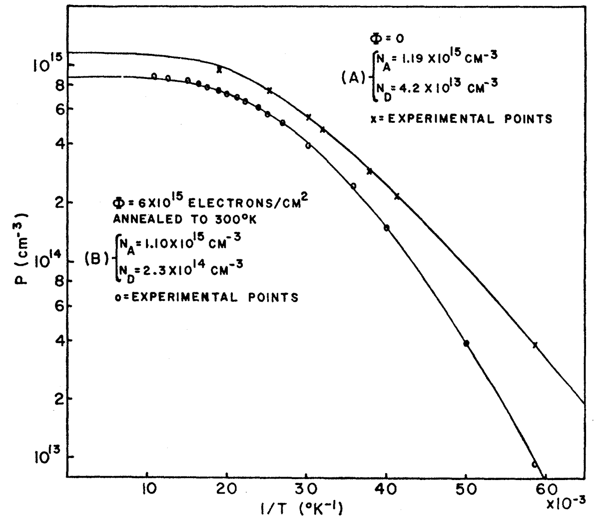

FIG. 10. Analysis of carrier-concentration curves before and after bombardment and annealing to room temperature. Changes in the acceptor concentration occur during breakup of the two-state defect.

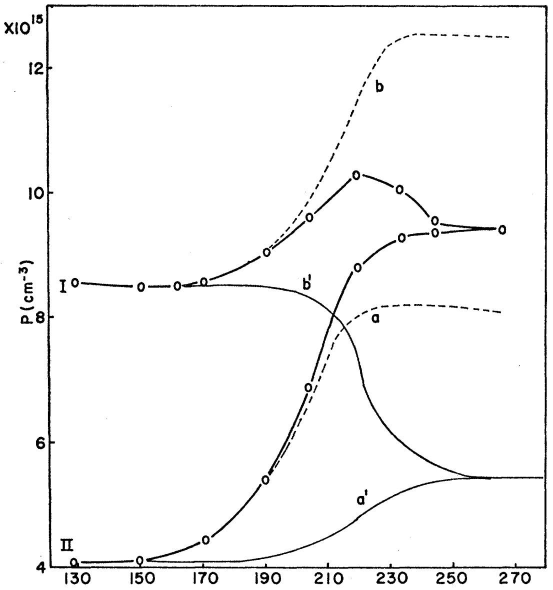

FIG. 11. The anomalous behavior of Ga-doped material. Curves through the experimental points can be decomposed into the normal breakup curves a' and b' plus a recovery stage, a and b, associated with the Ga.

necting the experimental points is an un-normalized plot corresponding to the same annealing which is depicted for other dopants in Fig. 9, with curve I corresponding to the (0) state and curve II to the (+) state of the defect. The normal breakup curves of Fig. 9 are superimposed on Fig. 11 as curves b' and a'. Subtracting b' and a' from curves I and II, respectively, a recovery stage designated by b and a remains. This stage can be fitted by first-order analysis to give an activation energy of 0.22 eV with an effective frequency of about 750 $\sec^{-1}$.

This recovery stage is apparently associated with the gallium impurity. If this is so, other anomalous recoveries might be expected for other dopants, but perhaps in different temperature ranges. In Fig. 12 the 100–150°K transformation is shown for three other doping materials. The lower curve, shown here for thallium-doped material, is the same shape for gallium- and indium-doped material as well. Boron-doped material shows an anomalous peak at about 125°K and aluminum-doped material at about 130°K. Annealing indium-doped specimens to 385°K produced no analogous peak.

V. SUMMARY

Lattice defects are introduced into *p*-type Ge at 10°K by 1-MeV electrons, although the defects cannot be detected electrically immediately after bombardment. It has been shown that the changes observed after irradiation, illumination with infrared light, and heating do not occur unless the material is exposed to damaging radiation. The changes which do occur after bombardment with damaging radiation are summarized in Fig. 13. Illumination with infrared light ($h\nu < E_g$) after bombardment with 1.0-MeV electrons reveals two types of defects, both of which appear as ionized donors following illumination. These defects are distinguished by the different rates at which they are ionized under illumination (cf. Fig. 1), and by the different temperatures at which the ionized defects anneal (cf. Figs. 4 to 6). The defects which are ionized during the short-time constant process, characterized by τ_1, and which anneal in the temperature range from about 40 to 55°K in their ionized state will be called type 1 defects for this discussion. Those associated with the long-time constant ionization, $\tau_2 = 6\tau_1$, and which anneal in the temperature range from about 50 to 70°K will be called type 2 defects. In both cases the defects anneal at a lower temperature in their ionized state (cf. Fig. 3). If the ionization of the defects by the infrared light is not complete, a transformation of the defects occurs in the temperature range from 100 to 150°K, the magnitude of which is dependent on the duration of the illumination. A two-state defect is found after heating to 150°K, and the number formed is largest when none of the type 1 and type 2 defects have been ionized by illumination. The two-state defects break up near 200°K leaving behind a number of defects which behave as donors. The final stage of annealing for material bombarded at low temperatures is the disappearance of these donors near 400°K, which has been studied by Brown *et al.*[8] Anomalous recovery stages which are associated with the impurities are also observed for germanium doped with boron, aluminum, and gallium. These are omitted from Fig. 13 for clarity.

VI. DISCUSSION

It is evident from these experiments and from the work of many others[2,8,10] that effects observed directly after irradiation as well as the behavior of defects accompanying annealing results depend on the charge state of the defects and of their environment in the

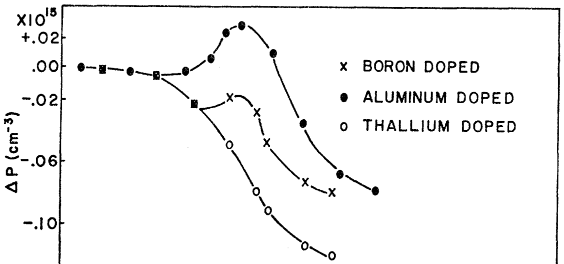

FIG. 12. Impurity-dependent annealing peaks for boron- and aluminum-doped samples. For these materials the anomalous behavior occurs during the 100–150°K transformation.

crystal. From the nature of n- and p-type material these charge states must be different, leading to different trapping properties for the migrating vacancies and interstitials and thus to different defect formations in the two types of material. Until more detailed knowledge is available of the different kinds of defect formations, the conditions under which migrations can occur, and when true annihilation of vacancies and interstitials takes place, a direct comparison of n-type with p-type behavior cannot be made. From a consideration of the results of our annealing, we can make a tentative model which will help us gain insight into the physical processes involved in the p-type material.

A. Annealing Results

If the annealing of the type 1 and type 2 defects seen in the 40–70°K recovery stages were only a retrapping of electrons by the defects, the recovery would return all of the defects to their un-ionized state, and further illumination would just repeat the trap-emptying process. Experimental results indicate that not only is retrapping not observed, but the illumination also has some influence on the number of two-state defects formed. It must therefore be concluded that atomic motion is involved in the recovery stages associated with the type 1 and type 2 defects.

Annealing of the ionized type 1 defect is either true recombination annealing or a change to a type of defect which is very resistant to ionization by illumination (cf. Fig. 6). If such a defect were formed in an occupied state as a result of heating, the carrier concentration would increase, producing a recovery like that associated with the ionized type 1 defect annealing.

The type 2 defect is probably quite similar to the type 1 defect structurally, since both the ionization behavior and the recovery stages associated with the ionized state are very similar. Both defects are susceptible to radiation annealing in their ionized state. There is also no evidence of further transformations after the 40–70°K recovery for either type of ionized defect. Hence, the annealing of the ionized defects may well be close-pair annealing.

That the formation of the two-state defects from defects produced at 10°K is related to the 40–70°K recovery and to the 100–150°K transformation is evident from the manner in which the magnitudes of the thermal changes are affected by the length of time of illumination (cf. Fig. 7). It is easily shown that the two-state defects are not found in material bombarded at 10°K before the 100–150°K transformation. After annealing the specimens to 80°K, a burst of ionizing radiation has no effect on the carrier concentration or the conductivity. Thus, the two-state defects are not present in the (+) state before the 100–150°K transformation. If they are present in the (0) state, they should give up their electrons during the 100–150°K transformation. Since the electron excitation from the two-state defect does not follow simple kinetics, the fact that pure first-order kinetics are observed for the 100–150°K transformation rules out the possibility of their existence in the (0) state. Confirmation is obtained from the fact that the thermal excitation of electrons from the two-state defects has an activation energy different from that of the 100–150°K transformation. The reasonable conclusion is that the two-state defects are formed as a result of the 100–150°K transformation.

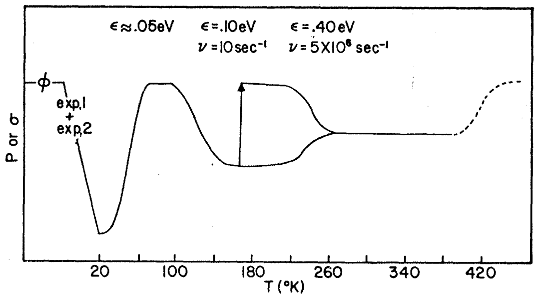

FIG. 13. Summary of effects observed in p-type Ge which has been irradiated at low temperature and annealed to near 400°K. Impurity-associated recovery stages are not included. The annealing near 400°K is described in Ref. 8.

Let us now examine the relationship between the number of un-ionized type 1 and type 2 defects and the number of two-state defects formed. Consider the simplest case; i.e., suppose all un-ionized defects of either type form two-state defects. Let the number of ionized defects be called N_i, the number of un-ionized defects N_0, and the total number of defects N, then

$$N=N_i+N_0. \tag{3}$$

For small changes in the carrier concentration

$$\Delta p=\alpha N,$$

then

$$\Delta p_{h\nu}=\alpha N_i \tag{4}$$

is the change in p produced by the ionization of the defects with infrared light, and

$$\Delta p_2=\alpha N_0$$

is the change in p due to the number of two-state defects, and

$$\sum\Delta p=\alpha N$$

is the change due to the total number of ionizable defects. Then from Eq. (3)

$$\Delta p_{h\nu}/\sum\Delta p+\Delta p_2/\sum\Delta p=1. \tag{5}$$

In Fig. 14, the line from $\Delta p_{h\nu}/\sum\Delta p=1$ to $\Delta p_2/\sum\Delta p=1$ represents the prediction of this simple model. The experimental points are obtained from Fig. 7 and curves like it for other samples. It is seen that the model works well for large $\Delta p_{h\nu}$ where Exp. 1 is complete. Hence, it appears that all un-ionized type 2 defects form two-state defects. The agreement begins to fail when $\Delta p_{h\nu}$ becomes small enough so that all the type 1 defects are

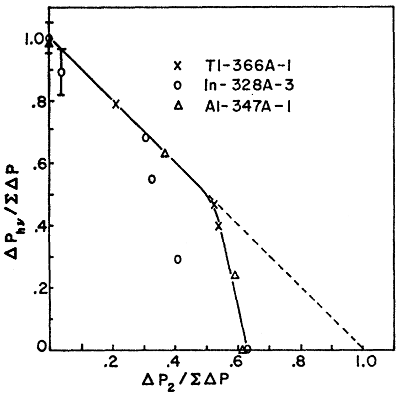

FIG. 14. Carrier-concentration changes produced by illumination compared to those produced by the two-state defect formation. For short illumination times the experimental points drop off too fast indicating that some un-ionized type defects do not form two-state defects.

not ionized. Thus, some of the un-ionized type 1 defects do not form two-state defects. In fact, for $\Delta p_{h\nu}=0$ only about 20% of the type 1 defects form two-state defects (the initial distribution is 60% type 1 and 40% type 2).

The two-state defect is a very puzzling defect, and just how its trapping properties come about is not yet clear. MacKay[11] has suggested that a likely configuration would be a complex defect in which a change of electronic state is accompanied by a structural change. The cycling between states could then follow a reversible diffusion reaction of the type,

$$(QP)^0 \leftrightarrows Q^{++}+P^{-}+e^{-}, \qquad (6)$$

where Q and P represent the components of the defect. It does not seem likely that P is an impurity. Whan[12] has irradiated n-type Ge with 2-MeV electrons at 25°K. The growth of absorption bands at 719 and 736 cm^{-1} were observed between 58 and 78°K. Further heating to 120°K resulted in the decay of those bands and the growth of one at 620 cm^{-1}. She concluded that all of these bands were associated with oxygen-defect complexes. It is probable that the material she used was converted to p-type by the irradiation and one might be tempted to identify our 40–70°K recovery stage and the two-state defect formation with the same oxygen-defect complexes since the temperature ranges are nearly the same. However, there is nothing in Whan's work that compares with the recyclable behavior of the two-state defect. The charge state in her samples will be much different than that in ours even though they may both be p-type. And finally, Trueblood[13] has observed two-state defect concentractions of about 3×10^{17} cm^{-3} in samples containing less than 10^{16} oxygen atoms per cm^3 and concentrations of about 10^{14} cm^{-3} for other impurities. Vook[14] finds two-state defect concentrations of about 10^{17} cm^{-3} for samples doped with about 10^{14} cm^{-3} impurities. There remains the possibility that P is an impurity which is undetectable by normal means, but it is difficult to see how it could be present in such large concentrations. The reaction (6) does seem a promising one, since Trueblood's spin-resonance measurements on the defect on the (0) state indicate that its structure is relatively simple.

Although some recombination of vacancies and interstitials may result from the breakup of the two-state defects, about 70% of the defects form donors on breaking up. These donors may be the result of the formation of complex defects such as divacancies, di-interstitials, or the trapping of defects at dislocations. Also, some of the defects form a type of complex with some of the substitutional impurities, altering their acceptor energy. Since what is observed is the breakup of the defect, the effective frequency is associated with the rate at which the defects are liberated from whatever structure gives rise to the two-state defect. Neither vacancies nor interstitials can be singled out at this stage as the liberated components in the two-state defect breakup. Although the migration energy of the vacancy in germanium is usually given as about 1 eV,[15] too high to allow a vacancy to migrate in this process, measurements of this quantity are complicated by the possibility of vacancy trapping. Watkins[16] gives 0.33 eV as the energy of migration for neutral vacancies in silicon from spin-resonance measurements. Since the migration energies reported by Benneman[15] for vacancies are all higher for Si than for Ge, Watkin's measurements indicate that the migration energy of a vacancy may be below 0.33 eV. Thus, the vacancy cannot be ruled out yet as a possible participant in the two-state defect breakup.

The impurity-associated recovery stage in boron-, aluminum-, and gallium-doped material, and the lack of such a recovery stage in indium-doped material, suggest an interstitial germanium-substitutional impurity replacement process. Some gain in strain energy could be expected if a germanium interstitial were to replace a smaller impurity in the lattice.[17] However, since interstitial impurities could no longer be expected to be acceptors, a decrease in the number of acceptors would be observed as a result of this recovery. Careful measurements of the carrier concentration versus temperature were made before and after the recovery in aluminum-doped material and analyzed using the method outlined in Sec. III. The acceptor concentrations were determined with an average deviation of

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[11] J. W. MacKay (private communication).

[12] R. E. Whan, Phys. Rev. **140**, A690 (1965).

[13] D. Trueblood, Phys. Rev. **161**, 828 (1967).

[14] F. L. Vook, Phys. Rev. **138**, A1235 (1965).

[15] K. H. Benneman, Phys. Rev. **137**, A1497 (1965).

[16] G. D. Watkins in *Proceedings of the International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), Vol. 3, p. 97.

[17] G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957), p. 138.

0.5%. It was found that for a recovery stage in which a 5% increase in the carrier concentration was observed, there was a 5% increase in the acceptor concentration. Similar increases were observed in boron-doped material, but the increase in the acceptor concentration was only slightly larger than the average deviation associated with the determination. In view of these measurements, a germanium-impurity replacement process seems unlikely.

Recent work by Hiraki *et al.*[18,19] shows that impurity atoms may be displaced by bombardment and the presence of these interstitial impurities can affect the annealing. As yet there are no results concerning the effect that *p*-type impurities might have in such displacements. In view of the fact that no impurity-dependent effects are found for thallium and indium, and since N_a does not decrease during bombardment, it seems unlikely that the impurity-dependent stages seen here are associated with the displaced impurity mechanism.

It is known that some substitutional impurity-interstitial impurity pairing occurs in semiconductors forming donor-acceptor complexes.[20] The impurity-dependent recoveries could then be due to the breakup of such impurity pairs. Since this recovery is always observed when a defect transformation is occurring, a migrating defect may influence the breakup.

B. Macroscopic Model

A macroscopic model for the lattice defects based on the above discussion is diagrammed in Fig. 15. The un-ionized type 1 and type 2 defects which are produced by the electron beam at 10°K are represented by the boxes marked D-1 and D-2, respectively. Illumination with infrared light causes each type to give up an electron with its characteristic exponential, resulting in ionized defects, shown as D-1′ and D-2′ in the diagram. The annealing temperature given after each ionized defect type is the temperature about which the recovery in dN_a/dT is centered in Fig. 4(b). The paths emerging from the left of the boxes D-1 and D-2 represent the transformations of the un-ionized defects when the lattice is heated. The disappearance of some of the un-ionized defects as the temperature is raised is shown by the dashed line leading to the "anneal" box. The remainder of the un-ionized defects follow the solid line, forming two-state defects. A representative temperature for the breakup of the two-state defect is also shown. The box marked "anneal" is not meant to imply true recombination annealing, but only a disappearance of a particular kind of defect.

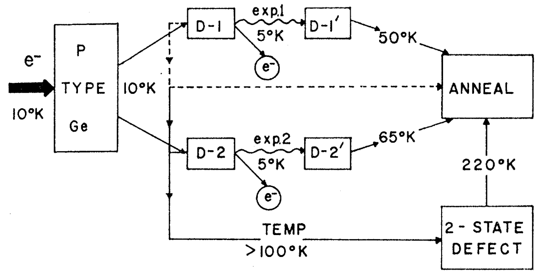

FIG. 15. A macroscopic model describing effects observed in bombarded *p*-type Ge.

C. Comparison with Degenerate Material

The foregoing results and conclusions are consistent with the findings of Klontz and MacKay.[1] After bombarding degenerate *p*-type Ge at 10°K with 1-MeV electrons, they produced a 1% decrease in the conductivity with infrared light. This decrease was erased with 1×10^{15} electrons/cm^2 at 0.315 MeV.

These results are similar to those of Whitehouse,[2] who bombarded degenerate *p*-type Ge with 4.5-MeV electrons. Illumination at 4°K ($h\nu<E_g$) following bombardment, produced a decay in the conductivity like the one observed for nondegenerate material. He also observed a recovery stage in the conductivity from 40 to about 80°K, referred to as *P*1, and a decrease in the conductivity from about 80 to 120°K, called *P*2. The process *P*1 was shown to be a first-order process and produced only a 50% recovery in the conductivity. Our 40–70°K recovery is complete to the initial value in both carrier concentration and conductivity. It also seems to be more complex than that of Whitehouse's *P*1 in that two separate recovery regions are noted for both the warming curve and isochronal annealing. The activation energy for our process and that of *P*1 are of the same order of magnitude. Process *P*2 is one in which the conductivity decreased between 80 and 120°K. The corresponding region for our experiments is from 100 to 150°K, but the comparison between our results for the 100–150°K transformation and process *P*2 seems very remote. Already at 80°K some of the two-state types of recyclable traps are apparent in *P*2 while we do not begin to see them until the temperature is greater than 100°K. Both isochronal and isothermal data show our transformation is first order while *P*2 is closer to a second-order process. There are several similarities in the two experiments but even more notable differences.

These differences are probably attributable to one or a combination of the following factors: energy, carrier concentration, length of irradiation. Whitehouse used 4.5-MeV electrons and observed a decrease in the conductivity during bombardment. Hence, some types of defects are introduced by 4.5-MeV electrons which are not seen with 1-MeV electrons. With regard to the second possible factor, he was using degenerate material, where the Fermi level is in the valence band.

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[18] A. Hiraki, J. W. Cleland, and J. H. Crawford, Jr., J. Appl. Phys. 38, (1967).

[19] A. Hiraki, J. W. Cleland, and J. H. Crawford, Jr., in Proceedings of the Santa Fe Conference on Radiation Effects in Semiconductors, Santa Fe, New Mexico, 1967 (to be published).

[20] B. I. Boltaks, *Diffusion in Semiconductors* (Academic Press Inc., New York, 1963), p. 188.

This could have influenced the stability of some kinds of defects. Finally the irradiations used were about a factor of 60 longer in time than those for the nondegenerate material reported in this paper. Radiation conversion of the defects is known to take place in *n*-type Ge,[21,22] and we have shown in this paper that ionized type 1 and type 2 defects are susceptible to radiation annealing. Hence, some of the defects in the degenerate material may have been altered by the electron beam. Experiments investigating the effects of the above three parameters on the defects formed could shed considerable light on the processes occurring in *p*-type Ge damaged at low temperatures.

D. Microscopic Descriptions

Construction of a microscopic model consistent with the effects observed cannot be uniquely determined from data from electrical measurements alone. A rather simplified model presents itself if it is assumed that at very low temperatures the defects are not sufficiently mobile to form complex associations, hence there is a high probability for vacancy-interstitial pair production. At temperatures near liquid helium, there is no evidence for any long-range migration in germanium, and 1-MeV electrons would be expected to produce defects which are primarily isolated vacancy-interstitial pairs. If it is assumed that there are two stable separations for such pairs, either of which may trap an electron, these configurations could give rise to the type 1 and type 2 defects observed. Since the mobility does not change significantly during bombardment, the pairs with their trapped electron must scatter holes like neutral centers. Under illumination the reaction

$$V^-I^+ \xrightarrow[h\nu]{} V^-I^{++}+e^- \tag{7}$$

would take place. Although this reaction goes at different rates for the two-defect types, the same reaction holds for both types. Under the increased Coulomb field when the defects are ionized,

$$(V^-I^{++})_1 \xrightarrow[T>40^\circ K]{} \text{annihilation}+\text{hole}, \tag{8}$$

where the interstitial is expected to do the jumping since the activation energy for motion of the interstitial should be lower than that for a vacancy. The type 2 defect is postulated to be the more widely separated pair. Before the reaction (8) can take place for the type 2 defects, we must have

$$(V^-I^{++})_2 \xrightarrow[T>50^\circ K]{} (V^-I^{++})_1 \tag{9}$$

and then reaction (8). The reaction (8) for the type 1 defects and the sequence of reactions (9) and (8) for the type 2 defects produce the 40–70°K recovery. Since only reaction (8) involves a charge carrier, only this reaction would be observed for the recoveries associated with both the type 1 and the type 2 defects.

If the samples are heated without illumination, the more closely spaced pairs, type 1, either become type 2 defects or recombine:

$$\begin{tikzcd} & \text{annihilation} & \\ (V^-I^+)_1 \arrow[ur] \arrow[dr] & & . \\ & (V^-I^+)_2 & \end{tikzcd} \tag{10}$$

The type 2 defects then follow

$$(V^-I^+)_2 \xrightarrow[T>100^\circ K]{} V^- + I^+. \tag{11}$$

Neither reaction (10) or (11) would be observable by carrier-concentration measurements. After reaction (11) there are two possible paths to the two-state defect of the form suggested in reaction (6). The liberated interstitial could give up an electron, producing the 100–150°K transformation, and then form the two-state defect D_{II},

$$\begin{aligned} \mathrm{I}^+ &\rightarrow \mathrm{I}^{++}+e^-, \\ \mathrm{I}^{++}+P^- &\rightarrow D_{\text{II}}^+. \end{aligned} \tag{12}$$

The other possibility is

$$\mathrm{I}^+ + P^- \rightarrow D_{\text{II}}^+ + e^-. \tag{13}$$

The reaction indicated by (13) seems less likely since the kinetics of excitation of the electron from the two-state defect are different from those of the 100–150°K transformation.

This model is, of necessity, rather speculative and whether it stands or falls rests on the results of future experiments.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Louise Roth for supplying the crystals used, to J. S. Raby for invaluable technical assistance, and to Professor J. W. MacKay for many helpful discussions and comments.

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[21] J. W. MacKay and E. E. Klontz, in *Symposium on Radiation Damage in Solids and Reactor Materials, Venice, 1962* (International Atomic Energy Agency, Vienna, 1963), Vol. III, p. 27.

[22] E. E. Klontz and J. W. MacKay, J. Phys. Soc. Japan **18**, Suppl. III, 1216 (1963).