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Low-temperature recovery of irradiation defects in n-type germanium*†

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Defect concentrations introduced into lightly doped n-type germanium by 1.0-MeV electrons at 7 °K have been monitored by measuring the hot carrier conductivity at 4.2 °K during a 0.66-μsec pulsed electric field of 100 V/cm and 1-sec duty cycle. Approximately 85% of the damage produced at 7 °K recovers in a thermal-annealing stage at 65 °K. Isochronal- and pulse-isothermal-annealing experiments, performed simultaneously on pairs of samples doped with approximately equal concentrations of different group-V impurities, show that the 65 °K annealing rate is dependent on the type of impurity. Radiation annealing was also studied by irradiating pairs of samples, damaged previously at 1.0 MeV, with low-energy electrons which produce little additional damage. The defects, which thermally anneal at 65 °K, radiation anneal at 7 °K with an annealing rate which is dependent on the type of group-V impurity dopant. This experiment suggests that one of the defects involved in these annealing processes is free to migrate over large distances near liquid-helium temperature. A model for the 65 °K stage is proposed in which the annealing is initiated by the breakup of an interstitial group-V impurity complex which was formed during 1.0-MeV irradiation. The interstitial is treated as a freely migrating particle which, when freed from the complex, can either migrate to a vacancy or be retrapped at an unoccupied impurity depending upon the relative charge states of these defects. From this model, it is possible to calculate the annealing rate of the 65 °K stage, the 7 °K-radiation-annealing rate, and the optical-annealing rates for optically stimulated annealing of the 65 °K defects at 4.2 °K during excitation with less-than-band-gap filtered light and at 30 °K during excitation with monochromatic light of energy greater than the band gap. This model also predicts an interstitial migration energy of 0.005 eV as well as a temperature-dependent radiation-annealing rate in the 5–15 °K temperature range in good agreement with recent data obtained by Hyatt and Koehler.

I. INTRODUCTION

Electrical measurements on n-type germanium irradiated with 1.0-MeV electrons near liquid-helium temperature indicate that acceptor levels are introduced below the Fermi level.[1–3] A thermal-annealing stage centered at 65 °K is the first recovery in conductivity to be observed in lightly irradiated samples, however, heavily irradiated degenerate material also exhibits recovery at 35 and 50 °K at the expense of recovery in the 65 °K stage.[2] In lightly doped material ($n_0 \approx 10^{14}$ cm^{-3}), the 65 °K stage is the only annealing to be observed below liquid-nitrogen temperatures, the recovery in this stage being as high as 95% for 0.7-MeV irradiations.[3] The 65 °K annealing is accompanied by a stored-energy release of about 5 eV per defect recovered.[4,5] Previous models for this annealing have assumed that vacancies and interstitials recombine during this stage in order to explain this large energy release.[4–12] These models have been reviewed by MacKay and Klontz.[13] Beyond this, agreement as to the nature of the 65 °K annealing stage diverges.[13]

MacKay and Klontz have suggested that close pairs of vacancies and interstitials recombine at 65 °K.[1] This model implies that the annealing kinetics for this stage should be first order. This is supported by Callcott's observation that samples doped with 10^{14} and 10^{17} Sb/cm^3 both anneal in the same temperature range during similar isochronal anneals.[3] If the annealing kinetics are described by a simple rate equation of the form

$$\frac{dN}{dt} = -K(T)N^n , \tag{1}$$

where N is the number of defects remaining, n is an integer defining the order of the reaction, and $K(T)$ is the temperature-dependent rate constant, then the fraction of defects remaining after a fixed annealing time can be independent of the initial defect concentration only if $n = 1$, i.e., first-order kinetics.

Annealing has also been observed near liquid-helium temperature during low-energy electron irradiation[1–3] or during less than band gap energy optical stimulation.[7] The fraction of defects recovered in these experiments near liquid-helium temperature is at the expense of the fractional recovery at 65 °K, the sum of the fractions recovered being a constant. The conclusion to be drawn is that annihilation, which is thermally activated at 65 °K, can be made to occur at less than 10 °K if the defects can be externally forced into charge states which favor defect recombination. If long-range defect migration near liquid-helium temperature is assumed not to occur, then a close-pair model, including a recombination probability which is charge-state dependent, seems to be the only

way to explain these liquid-helium annealing experiments.

Zizine[5,6] has reported, however, that the annealing kinetics of the 65 °K stage are not consistent with a close-pair model. He observed that the fraction of defects annealed at 66 °K is proportional to $t^{-1/2}$ for long annealing times where t is the annealing time at this temperature. He has proposed that diffusion-controlled recombination of correlated vacancy-interstitial pairs occurs in this stage. He gives no explanation for the radiation annealing or optical annealing of these same defects at less than 10 °K with this model.

It is instructive to compare these two models with the more direct information, obtained from EPR and optical measurements, on irradiation defects in silicon. Although at least a dozen different defect structures have been identified, along with partial identification of a similar number, no vacancy-interstitial pairs or isolated silicon interstitials have been observed.[14] These experiments do not disprove the existence of these defects in germanium; however, it is perhaps more reasonable to construct models for the annealing stages in germanium in terms of defects which are known to exist in similar materials. Watkins[15] has proposed that the silicon interstitial can migrate over large lattice distances at less than 10 °K in order to explain his observation from EPR data that silicon vacancies and aluminum interstitials are produced in equal concentrations during liquid-helium electron irradiations. Since direct displacement of aluminum interstitials is very unlikely, he proposed that silicon interstitials migrate to impurity sites and displace substitutional aluminum atoms thereby producing the observed concentration of aluminum interstitials.

Vook has proposed that the 65 °K annealing stage in Ge might be explained by impurity trapping and that Ge interstitials can perhaps interact with impurities at temperatures as low as 4 °K.[16] MacKay and Klontz[17] have suggested that the concentration dependence in the 65 °K annealing observed by Zizine[5,6] could be the result of a difference in *type* of impurity used to dope his samples.

Koehler and McKeighen have made a direct attempt to measure the silicon-interstitial migration energy at 1.6 °K.[18] They conclude that this energy is less than 0.002 eV in silicon. They have proposed that the silicon interstitial migrates athermally during irradiation. Bourgoin and Corbett have proposed a mechanism for athermal interstitial migration in tetrahedral group-IV semiconductors which is based upon the idea that the interstitial equilibrium position depends on the charge state of the interstitial.[19]

A recent theoretical calculation of the interstitial equilibrium position dependence on charge state for the carbon interstitial in diamond lends support to the Bourgoin mechanism.[20] Hyatt and Koehler have measured an activation energy of 0.0044 eV associated with radiation annealing of the 65 °K defects in n-type Ge near liquid-helium temperatures. It is difficult to explain the source of this activation energy without invoking a freely migrating interstitial model.

In Sec. III we will present experimental data which suggest that germanium interstitials are interacting with impurities at near liquid-helium temperatures. Although some of these data have been presented previously,[12] Figs. 4, 7, and 9 are presented again in this paper for completeness. We have previously found that the 65 °K annealing rate and also the 7 °K radiation annealing rate are both dependent on the type of group-V doping impurity.[12] These experiments indicated that a departure from vacancy-interstitial pair models was an appropriate step to take in explaining radiation effects in germanium. A qualitative discussion of the reasons for this new model are found in Ref. 12. In Sec. IV, an approximate mathematical model for the 65 °K annealing stage will be presented for the first time based on this point of view. The charge states of the interstitial, the vacancy and the group-V impurity are explicitly taken into account. The frequency factor for the thermal annealing at 65 °K is calculated using this model. In Sec. V, using the mathematical model presented in Sec. IV, the annealing rate constants for radiation annealing and optical annealing at less than 10 °K and the optical annealing at 30 °K are also calculated and compared with experiment for the first time. With this model, most of the observed annealing data for lightly doped n-type germanium can be explained quantitatively.

II. EXPERIMENTAL PROCEDURE

The experiments to be described were performed on uncompensated Sb-doped, P-doped, and As-doped germanium samples. Exhaustion-range carrier concentrations were within 1.5×10^{14} cm^{-3} to 5.5×10^{14} cm^{-3} for all the samples. The carrier concentrations, obtained from dc Hall-effect measurements at 77 °K are listed in Table I. Samples were sliced from x-ray orientated single crystals. The largest face, a $\{110\}$ plane, was the surface irradiated in all cases. Samples were ground and then etched in CP4 solution to a final thickness of 0.1 mm. Samples were then mounted in the same metal cryostat in which the irradiations were made. The design of this exchange-gas cryostat is described elsewhere.[3,21] The dc conductivity and Hall coefficient were again measured at 77 °K. Sample temperatures were measured with a $\frac{1}{8}$-W 470-Ω carbon resistor.

TABLE I. Samples used in annealing experiments.

Experiment	Sample	77 °K carrier concentration before irradiation (e^-/cm^3)
1[a]	Ge(As)-140A-1	1.58×10^{14}
2[a]	Ge(Sb)-268A-1	3.33×10^{14}
3	Ge(As)-353A-2	4.65×10^{14}
	Ge(Sb)-263A-1	3.33×10^{14}
4[b,c]	Ge(As)-453A-3	5.52×10^{14}
	Ge(Sb)-441A-1	4.98×10^{14}
5	Ge(As)-453A-2	4.65×10^{14}
	Ge(P)-440A-0	2.32×10^{14}

[a]Irradiated and annealed in separate experiments (all other experiments done on pairs of samples).

[b]Sample positions reversed in cryostat from previous experiment.

[c]Radiation annealing and pulse isothermal annealing on this pair of samples.

Irradiations were made using a 1.0-MeV Van de Graaff electron accelerator. The electron beam was scanned in both vertical and horizontal directions before entering the cryostat sample chamber through a 0.001-in. Al window on the exchange-gas can. Irradiations were made in all cases with sample temperatures below 10 °K. Irradiation and annealing experiments were always made with the samples in a dark environment. This is necessary because the 65 °K annealing stage can be optically annealed at much lower temperatures.[6,7,22] An analyzing magnet defined the electron-beam energy to an accuracy of ±3%. The irradiation rates used were less than 6×10^{11} e^-/cm^2 sec (0.1 $\mu A/cm^2$). Beam current was monitored continuously during irradiation by collecting the beam electrons on a scattering shield in the exchange-gas can and on a Faraday cup on the nitrogen shield. Fluences were measured to an accuracy of ±10%.

Pulse conductivity was used to monitor the damage introduced by irradiation. This hot-carrier measurement has been described in detail by Callcott.[3] We give here only a brief description of the technique. Voltage pulses were obtained by discharging a length of coaxial cable through a mercury-wetted reed relay into a matched load. The pulse length was 0.66 μsec with a pulse rate of 1 pulse per sec. Sample current was along the ⟨110⟩ direction. Pulse conductivity was measured as a function of applied electric field by observing the voltage pulses at two voltage probes on the sample; pulsed sample current was determined by the voltage drop across a standard resistor in series with the sample. These pulse voltages were measured with a type 545 Tektronix oscilloscope and a type-W preamplifier. Voltage pulse heights from 10 to 300 V could be measured to a relative accuracy of 0.5%.

During a 0.66-μsec pulse at 100 V/cm the lattice temperature rise is no more than 5 °K while the electron "temperature" is well above that required for complete ionization of the donor impurities.[3]

Callcott[3] has shown that for electric fields greater than 70 V/cm, the effects of charged impurity scattering become negligible. In this case

$$\Delta\sigma/\sigma_0 \approx \Delta n/n_0 ,$$

where $\Delta\sigma/\sigma_0$ is the relative change in conductivity at an electric field of 100 V/cm and $\Delta n/n_0$ is the relative change in the carrier concentration due to irradiation. Callcott has also shown that the defect which anneals at 65 °K is a double acceptor, i.e., each defect removes two electrons from the conduction process.[3] Therefore, by measuring the change in conductivity at a constant field of 100 V/cm, we have a parameter $\Delta\sigma$, which is proportional to the number of double acceptor defects.

Since an impurity dependence in the annealing rates for samples doped with different types of impurities has been observed, it was important to check that the impurity effects are not a characteristic of the hot-carrier measurement. This was done by noting that $\Delta\sigma/\sigma_0$ approached a constant value at the same electric field in samples doped with different types of dopant. In all experiments to be described in Sec. III, conductivity was always measured at 100 V/cm. Conductivities measured at this field are analogous to dc conductivity measurements in the exhaustion temperature range and are therefore independent of the effects of carrier freezeout.

III. EXPERIMENTAL RESULTS

A. Isochronal annealing

A preliminary set of isochronal annealing experiments were performed to search for an impurity dependence in the 65 °K annealing rate. Defects were introduced into pairs of samples, each sample being doped with a different type of group-V impurity but in equal concentrations, by irradiating with 1.0-MeV electrons. The sample temperature was less than 10 °K during irradiation. After irradiation, samples were heated to 15 °K in order to fill all the double acceptor defects with electrons. This is necessary because a nonequilibrium electron distribution can exist at 4.2 °K immediately after irradiation.[3]

The pulse conductivity of the samples, with all the double acceptors fully occupied, was measured at 4.2 °K in order to monitor the bombardment damage. Samples were irradiated until a 20–30% decrease in conductivity at 100 V/cm was obtained. The temperature of the samples was then raised to the annealing temperature for 700 sec and returned to 4.2 °K for a conductivity measurement. This was repeated at approximately 3° temperature intervals until the conductivity failed to recover further.

Table I lists the samples used in the five isochronal annealing experiments. Experiments 1 and 2 were performed on separate samples; all other experiments were performed on sample pairs. In experiment 4, the mounting positions of the samples were reversed from those positions used in the other experiments. In experiment 5, a P-doped sample was compared with the As-doped sample used in experiment 4.

The results of these experiments are shown in Fig. 1. Not all the data points are shown. Since the total recovery in all the samples was approximately 85%, the recoveries have been normalized in this figure so that the fractional recovery in conductivity at 100 °K is taken as 1.0. In all cases, the As-doped samples annealed at a lower temperature than the Sb-doped samples. The rate of recovery for the P-doped sample was greater than the recovery for the Sb-doped sample but less than that of the As-doped sample. The impurity dependence is strongest at the beginning of the anneal. The As-doped samples reached 5% recovery about 5 °K lower in temperature than the Sb-doped samples; at 50% recovery this difference in temperature is only about 2.5 °K. This same behavior is seen in the pulse isothermal annealing experiments and in the radiation annealing experiment discussed below. It is apparent that the type of impurity is affecting the annealing rate in some manner.

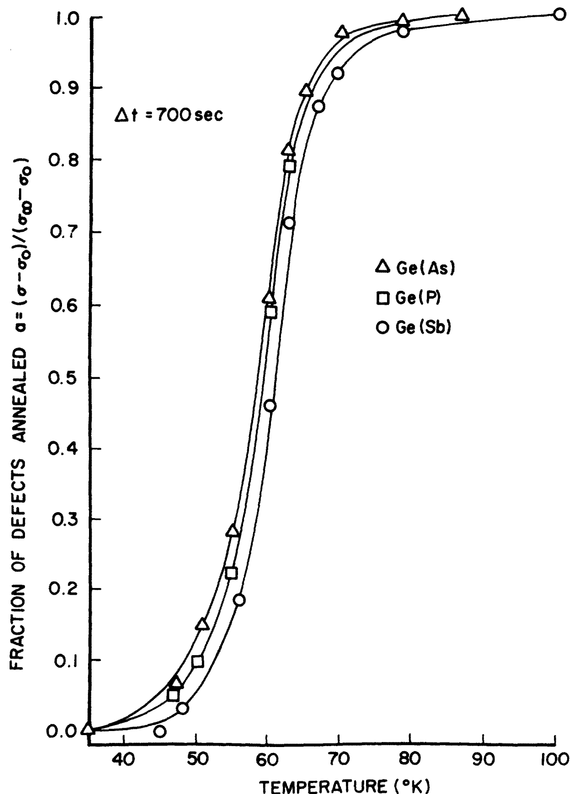

FIG. 1. Isochronal anneals for samples doped with different group-V impurities. Temperature pulse lengths were 700 sec.

B. Pulse isothermal annealing

Pulse-isothermal-annealing experiments were performed on the pair of samples Ge(As)-453*A*-3 and Ge(Sb)-441*A*-1 in order to examine the annealing kinetics quantitatively. These two samples were irradiated and annealed as a pair. The initial carrier concentrations at 77 °K were matched to within 10% as is shown in Table I. These samples were irradiated at less than 10 °K until a 25% decrease in conductivity occurred. They were then annealed simultaneously by heating the sample chamber to the same annealing temperature for increasing lengths of time. The annealing procedure used in this case is commonly known as pulse annealing. The pulse conductivity was always measured at 4.2 °K between temperature pulses. After an isothermal anneal at a particular temperature was completed, the samples were warmed to 300 °K overnight before the next isothermal run was made. This removed most of the damage not annealed at 65 °K. Then the pair was again irradiated at 4.2 °K to approximately the same defect concentration used in the previous run. Annealing was then observed at a different temperature. The order in which the anneals were made was 54, 58, 62, 50, 56, 60, and 52 °K.

Figures 2 and 3 show the fraction of defects remaining as a function of annealing time at a particular temperature for the Sb-doped and As-doped samples, respectively. This fraction f is defined as

$$f = [\sigma(\infty) - \sigma(t)]/[\sigma(\infty) - \sigma(0)], \qquad (2)$$

where $\sigma(0)$ is the initial conductivity before annealing, $\sigma(t)$ is the conductivity after annealing at the indicated temperature for time t, and $\sigma(\infty)$ is the conductivity obtained after heating the samples to 100 °K for 7 min at the end of the annealing run.

In Fig. 4, the impurity dependence is illustrated by comparing annealing runs at 50, 52, 54, and 58 °K for the two samples.[12] The As-doped sample anneals more rapidly than the Sb-doped sample as was observed in the isochronal anneals. The impurity dependence is strongest at early annealing times and lower annealing temperatures. For longer times, the annealing curves for the two samples parallel each other indicating that the impurity effect has saturated. At 60 °K, there is no detectable difference between the two samples to within experimental error.

The fraction of defects remaining is found to be proportional to $t^{-1/2}$ at longer annealing times in

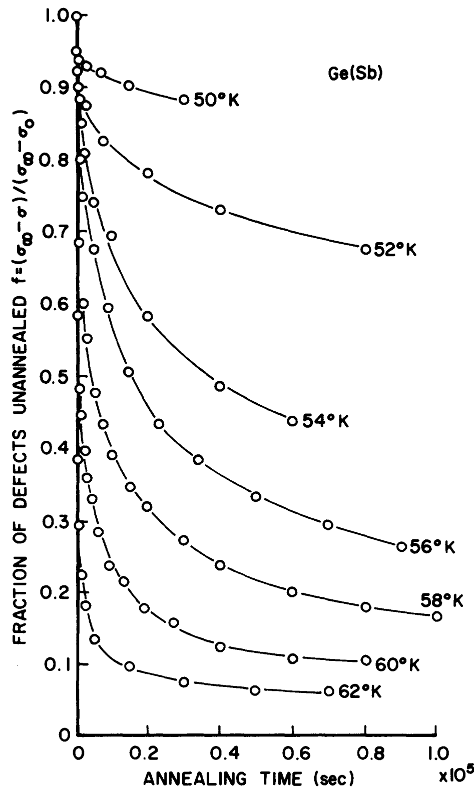

FIG. 2. Pulse isothermal anneals for Sb-doped germanium in the temperature range 50–62 °K.

agreement with the results reported by Zizine for more heavily doped samples.[5,6] This is illustrated in Figs. 5 and 6 for the Sb-doped sample where $1/f^2$ is plotted versus the annealing time. The fraction of defects not annealed f is defined by Eq. (2). The results are similar for the As-doped sample. From Figs. 5 and 6, it is apparent that

$$f \approx (Kt+1)^{-1/2}, \tag{3}$$

where K is the effective rate constant and has units of reciprocal time. By plotting $\ln K$ vs T^{-1}, where T is the annealing temperature, we find that

$$K = K_0 e^{-E_a/kT}, \tag{4}$$

where E_a is the activation energy associated with the longer annealing times, k is Boltzman's constant, and K_0 is the effective frequency factor. We find that the activation energies and effective frequency factors associated with the $t^{-1/2}$ annealing kinetics are the same for both samples to within experimental error, i.e., $E_a = 0.15 \pm 0.01$ eV and $K_0 = (3 \pm 2) \times 10^{10}$ sec^{-1}. This result agrees with our conclusion that the type of impurity is not affecting the annealing rate at the longer annealing times.

C. Radiation annealing

The defects which thermally anneal in the 65 °K stage can be annealed near liquid-helium temperature by irradiation with electrons whose energy is below the germanium atom displacement threshold. This radiation annealing has been observed in nearly degenerate samples[1] and in nondegenerate samples.[3] We have observed that this radiation annealing at less than 10 °K is dependent on the type of impurity dopant.[12]

Samples Ge(As)-453A-3 and Ge(Sb)-441A-1 were damaged with 1.0-MeV electrons until the conductivity at 100 V/cm decreased 29%. The pair of samples was then irradiated with 500-keV electrons. The samples's temperatures were observed to rise to approximately 7 °K during this irradiation. The beam intensity (flux) was 1.25×10^{11} $e^- \text{cm}^{-2} \text{sec}^{-1}$. Figure 7 shows the recovery versus fluence (integrated flux). The As-doped sample recovers more rapidly than the Sb-doped sample. We observed almost no impurity dependence when the samples were radiation annealed at higher levels of ionization obtained by increasing the beam intensity or lowering the irradiation energy. This behavior is completely analogous to the thermal annealing behavior near 65 °K where the higher

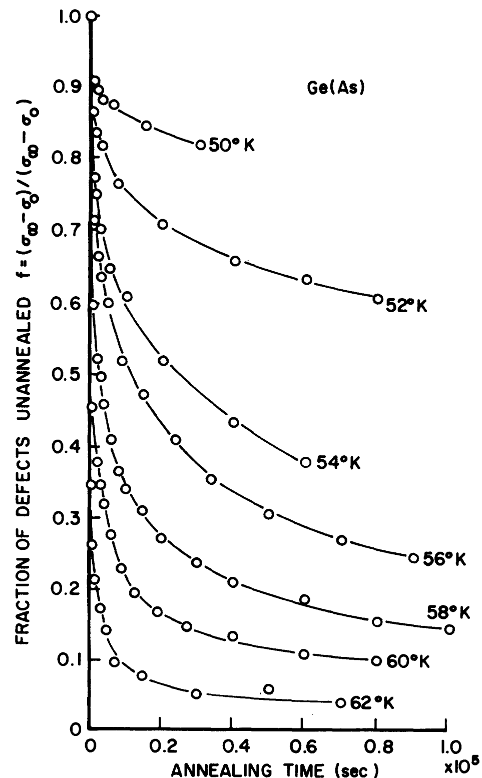

FIG. 3. Pulse isothermal anneals for As-doped germanium in the temperature range 50–62 °K.

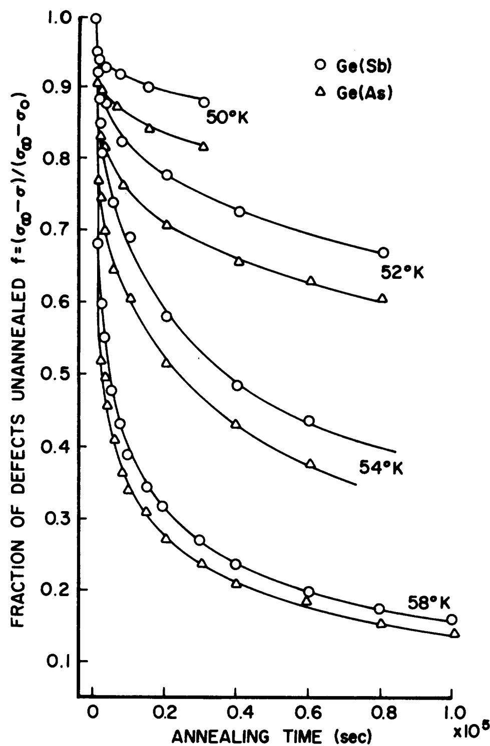

FIG. 4. Comparison of isothermal anneals for a pair of As- and Sb-doped samples irradiated and annealed simultaneously. The carrier concentrations in these samples at 77 °K before irradiation were 5.5×10^{14} cm^{-3} and 5.0×10^{14} cm^{-3}, respectively. Data are taken from Ref. 12.

temperature annealing was observed to be impurity independent.

The annealing kinetics for the radiation annealing are also similar to the 65 °K thermal annealing kinetics.[11,12] The fraction of defects remaining f is proportional to $\phi^{-1/2}$, where ϕ is the fluence (e^- cm^{-2}). For a constant beam intensity, $d\phi/dt = 1.25\times10^{11}$ e^- cm^{-2} sec^{-1}, the fluence is proportional to the annealing time. Then the slope of a $1/f^2$-vs-ϕ plot represents the effective cross section $S = 9\times10^{-15}$ cm^2 for radiation annealing. The annealing can again be represented by Eq. (3), where now, the effective rate constant obtained is

$$K=\frac{d\phi}{dt}S=11.2\times10^{-4}\,\mathrm{sec}^{-1}. \quad (5)$$

In Sec. V, a discussion of the significance of this rate constant as well as the effective rate constants for the thermal and optical annealing will be presented.

IV. NEW ANNEALING MODEL

The radiation annealing experiment described in Sec. III suggests that one of the defects produced during 1.0-MeV irradiation can migrate at 7 °K over sufficiently large distances so that defect-impurity interactions can occur.[12] If we assume that the migrating defect is the germanium interstitial, then these conclusions are consistent with the models for interstitial migration in Si.[15,23]

During irradiation, defects are produced under conditions which are similar to those which exist during radiation annealing. If interstitials migrate easily during radiation annealing, then they must also migrate during 1.0-MeV-electron bombardment. The large stored energy release and the high conductivity recovery which accompany annealing at 65 °K suggest that most of the interstitials produced during irradiation are temporarily trapped somewhere in the lattice and are released during annealing to annihilate vacancies. We will assume that the most likely trapping sites are at

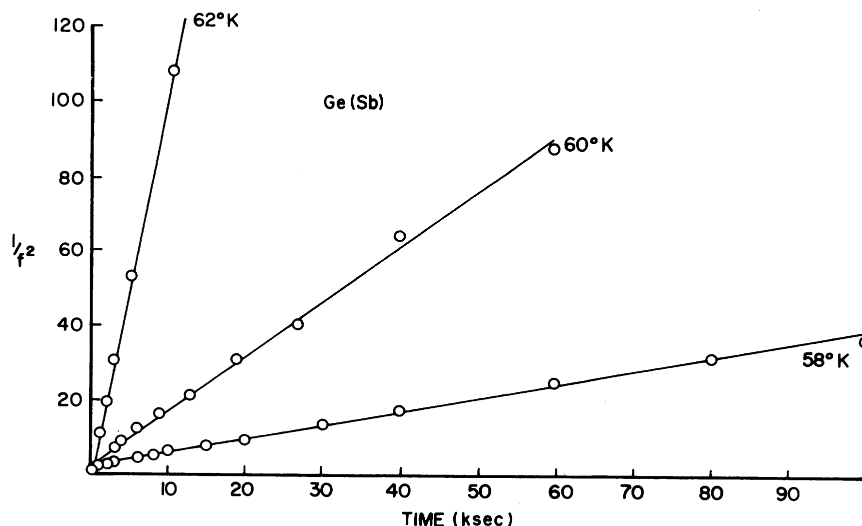

FIG. 5. Plot of the reciprocal of the square of the fraction of defects remaining vs time for Sb-doped Ge in the temperature range 58–62 °K. The relation $f\propto t^{-1/2}$ holds for an appreciable part of the anneal. Data are taken from Fig. 2.

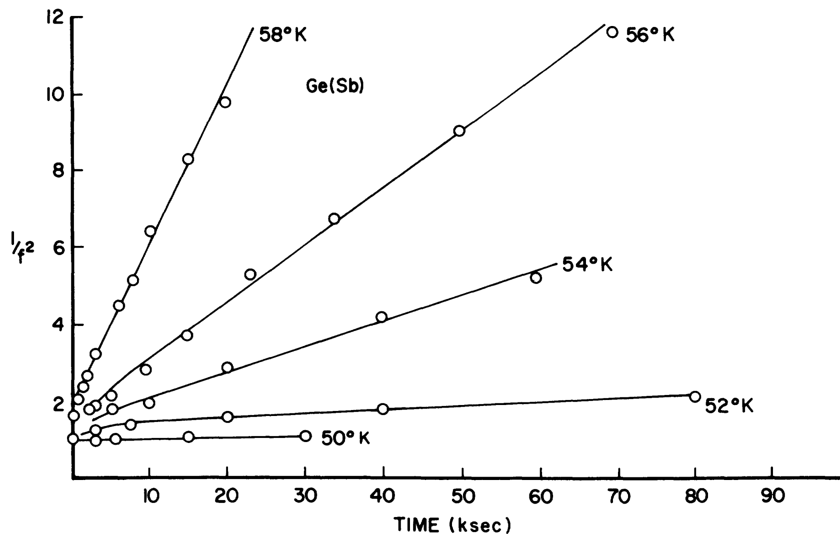

FIG. 6. Plot of the reciprocal of the square of the fraction of defects remaining vs time for Sb-doped Ge in the temperature range 50–58 °K. Data are taken from Fig. 2.

the group-V impurities. We propose that interstitial-group-V impurity complexes are formed during irradiation. Assuming that most of these interstitials are neutral during irradiation, because of the large numbers of electron-hole pairs generated by the electron beam, then the capture cross section for neutral interstitials at the impurity sites must be much larger than the cross section for annihilation of neutral interstitials at vacancy sites. We therefore expect the concentration of complexes formed during irradiation to be equal to the concentration of vacancies.

Radiation annealing and optical annealing experiments indicate that the charge states of the vacancies, interstitials and impurities are important in

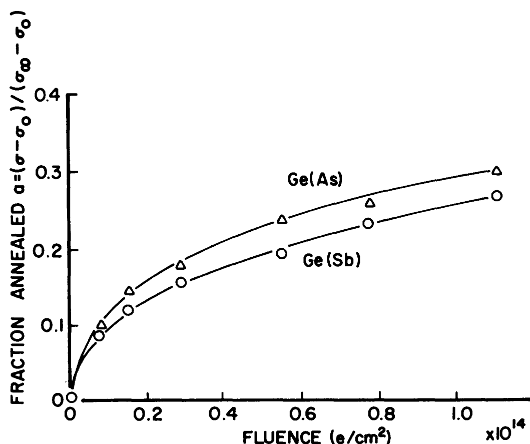

FIG. 7. Impurity dependence of the radiation annealing of 65 °K defects at 7 °K using a 500-keV electron beam of intensity 1.25×10^{11} e^- cm^{-2} sec^{-1}. Both samples were damaged and then annealed simultaneously. Data are taken from Ref. 12.

determining the rate of annealing the 65 °K defects.[1–13] These charge states are not in general known experimentally. We do know that the group-V substitutional impurity, Sb, for example, can exist in two charge states (Sb^0, Sb^+). Callcott has shown that one of the defects produced by 1.0-MeV irradiation is a double acceptor.[3] It is reasonable to assume that this defect is a vacancy which has captured two electrons to complete the dangling bonds of the neighboring Ge atoms. We will also assume that vacancies are always acceptors and interstitials are donors in n-type Ge. Then vacancies can exist in only three charge states (V^0, V^-, V^{--}). The free interstitials not bound in complexes will have only two charge states (I^0, I^+). The charge state of the complex should be commensurate with the above charge assignments, however, we assume that double donor complexes do not exist since under these conditions a Coulomb repulsion exists between the ionized interstitial and the ionized impurity.

On the basis of these charge assignments, it is possible to decide which defect interactions are most likely. We expect a Coulomb attraction between V^{--} and I^+ as well as between V^- and I^+. This Coulomb attraction favors annihilation by increasing the cross section for capture of the free interstitials at the vacancy sites. A Coulomb repulsion between I^+ and Sb^+ decreases the probability for complex formation. We therefore assume that the capture of a positive interstitial by a negative vacancy is more likely than the capture of a neutral interstitial. Likewise, the capture of a neutral interstitial by a positive impurity is more likely than the capture of a positive interstitial. In the model to be presented, we will neglect completely the less likely capture processes.

It is now possible to describe the annealing kinetics with a set of coupled differential rate equations which describe the concentrations of the various defects as functions of time. There will be one differential equation for each defect charge state as well as an equation for the concentration of electrons and an equation for the concentration of holes. This description yields a system of nine coupled nonlinear differential equations with a host of unknown rate constants. This system can, however, be greatly simplified if we make the assumption that the electrons and holes are always in thermal equilibrium with the defects during the anneal. This is justifiable since the lifetimes for excess carriers in a sample containing appreciable defects is of the order of μsec or shorter, however, the annealing times are of the order of thousands of seconds, or some 10^9 times slower. The system of equations can also be simplified because the defect concentrations are not independent. The total vacancy concentration V is equal to the sum of the concentrations of vacancies in all the possible charge states, i.e., $V=V^0+V^-+V^{--}$, where V^0 is the concentration of vacancies in the neutral charge state, etc. Likewise, $I=I^0+I^+$, where I is the total concentration of interstitials not bound to complexes (free interstitials). Then, assuming that interstitials are not lost to sinks other than vacancies or complexes, $V=I+C$, where C is the concentration of interstitial impurity complexes (bound interstitials). We are left with the following set of coupled equations:

$$\frac{dC}{dt}=-K_1C+K_2(i_0-C)I, \tag{6}$$

$$\frac{dV}{dt}=-K_3IV, \tag{7}$$

$$V=I+C, \tag{8}$$

where i_0 is the concentration of group-V impurities.

The rate constant K_1 is the probability per unit time for complexes to breakup and release interstitials. The constant K_2 is given by

$$K_2=P_I(0)\sigma_c v_I, \tag{9}$$

while K_3 is described by the equation

$$K_3=[P_I(+1)P_v(-1)\sigma_{v(-1)} + P_I(+1)P_v(-2)\sigma_{v(-2)}]v_I, \tag{10}$$

where v_I is the interstitial thermal velocity, σ_c is the capture cross section for capturing a neutral interstitial at a group-V impurity site, and $\sigma_{v(-q)}$ is the capture cross section for capturing a positive interstitial at a vacancy of charge q ($q=-1, -2$). The quantity

$$P_I(r)=I^{(r)}/I, \quad r=0, +1 \tag{11}$$

is the probability that the interstitial has a net electronic charge r, while

$$P_v(s)=V^{(s)}/V, \quad s=0, -1, -2 \tag{12}$$

is the probability that a vacancy has a net electronic charge s. The total concentration of free interstitials, $I=\sum_r I^{(r)}=I^0+I^+$, is the sum of the concentrations of free neutral interstitials and free positive interstitials. Likewise, $V=\sum_s V^{(s)}=V^0+V^-+V^{--}$ represents the total vacancy concentration.

Equations (6)–(8) can not be integrated in closed form unless $K_2=K_3$. We do not expect this restrictive condition to be satisfied in systems in which the defect charge states affect the annealing rates since, in Eqs. (9) and (10), $\sigma_c\neq\sigma_{v(-1)}\neq\sigma_{v(-2)}$ and also $P_I(r)$ and $P_v(s)$ are very different in magnitude for different charge states.

The hot-carrier measurements described in Sec. II were used to measure the relative concentrations of double acceptor defects which we have assumed to be vacancies. Therefore, we are interested in approximate solutions to Eqs. (6)–(8) for $V(t)$, the total vacancy concentration. Two approximations will be discussed. If we assume that retrapping of interstitials at impurity sites is very large, this condition will lead to a quasi-steady-state for the cencentration of complexes which is valid for very long annealing times. We will call this the steady state approximation. The second approximation assumes that the first term in Eq. (6) is much larger than the second. This represents a physical situation in which retrapping of interstitials at impurity sites can be neglected. Since we have assumed that all the interstitials which are released during the anneal were trapped at group-V impurity sites initially, then at $t=0$, the free interstitial concentration is zero making the second term in Eq. (6) negligible for short annealing times. We will call this approximation the transient solution.

A. Steady-state solution

We begin by substituting $I=V-C$ from Eq. (8) into Eqs. (6) and (7). By assuming a quasi-steady-state for the concentration of complexes ($dC/dt\approx 0$), we obtain a quadratic equation for C, and also assuming that $K_1/K_2\ll i_0$ so that the probability for retrapping is large, we obtain

$$C=\tfrac{1}{2}(V+i_0)(1-\{1-4(V/i_0)[1+(V/i_0)]^{-2}\}^{1/2}).$$

This same result is obtained if, instead of $dC/dt\approx 0$, we assume that the interstitial concentration is in quasi-steady-state ($dI/dt\approx 0$) and also that $K_2\gg K_3$ as well as the previous condition, $K_2\gg K_1$. We further approximate by assuming $V\ll i_0$ so that we may apply the binomial expansion to the above equation and retain only the leading term. This yields $C\approx i_0V/(V+i_0)$, or that $I=V-C\approx V^2/i_0$. When this expression is substituted into Eq. (7), we ob-

tain a differential equation for $V(t)$ which is third order, i.e.,

$$\frac{dV}{dt} \approx -\frac{K_3}{i_0} V^3 .$$

The approximations using $V \ll i_0$ are valid for longer annealing times in all the cases to be considered since in these experiments the maximum value of V was less than $0.15\, i_0$ at the beginning of the anneals.

Upon integration of the above differential equation, and using the initial condition $V = V_0$ at $t=0$, we obtain the solution for the fraction of vacancies remaining,

$$f = V/V_0 \approx [1 + (2K_3V_0^2/i_0)t]^{-1/2} . \qquad (13)$$

This solution is identical in form to Eq. (3) which described the experimental results for the 60 °K thermal annealing at long annealing times.

B. Transient solution

A second useful approximation is obtained by neglecting the retrapping term in Eq. (6). We obtain immediately the set of coupled equations

$$\frac{dC}{dt} \approx -K_1 C , \quad \frac{dV}{dt} = -K_3 V(V-C) .$$

Since all the interstitials are initially trapped at complexes, then $C_0 = V_0$ at $t=0$, and we obtain at once the solution for $C(t)$,

$$C(t) = V_0 e^{-K_1 t} .$$

After making the substitutions $y = V^{-1}$, $x = K_3 t$ and $C(x) = e^{-(K_1/K_3)x}$ into the differential equation for V, we obtain an equation for $y(x)$,

$$\frac{dy}{dx} + C(x) y = 1 .$$

This equation can be integrated using the integration factor $\exp[\int C(x)dx]$ to yield

$$y e^{-u} - y_0 e^{-u_0} = \int_{x=0}^{K_3 t} dx\, e^{-u(x)} = \frac{K_3}{K_1} \int_u^{u_0} u^{-1} e^{-u}\, du ,$$

where $u = u_0 e^{-K_1 t}$, $u_0 = (K_3 V_0/K_1)$, $y_0 = V_0^{-1}$ at $t=0$ and $y = V^{-1}$ at $t \neq 0$. The transient approximation for the fraction of vacancies remaining is now found immediately to be

$$f = \frac{V}{V_0} = \frac{e^{-(u-u_0)}}{1 + u_0 e^{u_0}[E_1(u) - E_1(u_0)]} , \qquad (14)$$

where again, $u = u_0 e^{-K_1 t}$, $u_0 = K_3 V_0/K_1$, and where

$$E_1(x) = \int_x^{\infty} p^{-1} e^{-p}\, dp$$

is the exponential integral and can be found tabulated in most math tables.[24]

V. COMPARISON OF MODEL WITH EXPERIMENTS

When comparing experimental annealing data with mathematical models, it is important to realize that reasonable fits to the data can be obtained for several quite different models by a suitable selection of the adjustable parameters in the models. For example, isothermal data obtained by Brown and Augustyniak[25] for room-temperature irradiated n-type Ge has been fit reasonably well both by Waite's correlated diffusion theory[26] and also by an approximate impurity trapping model presented by Spitsyn and Smirnov.[27] Our problem of selecting a model for the 65 °K annealing stage in this same material is analogous. The final decision must be based on experimental evidence other than the annealing kinetics at 65 °K. A direct approach to this problem is to estimate the magnitudes of the adjustable parameters of a particular model from first principles and to compare these estimates with experimental results. In the remainder of this section, we will attempt this comparison by making estimates of those rate constants which can be obtained experimentally from the two approximate solutions presented in Sec. IV.

The steady-state solution described by Eq. (13) yields the parameter $2K_3V_0^2/i_0$ which represents the effective rate constant for long annealing times where this approximation is appropriate. The constants V_0 and i_0 are known approximately from fluence and removal rate and from Hall measurements at 77 °K. The constant K_3, as defined in Eq. (10), is composed of terms which can be estimated once experimental information about the defect charge states is known.

The transient solution described by Eq. (14) depends on the parameters $u_0 = K_3V_0/K_1$ and K_1. A calculation of K_3 is again needed in order to compare the experimental and calculated parameters of the problem. By proposing a mechanism for the breakup of the impurity defect complexes, it should also be possible to calculate K_1.

Neither approximation can yield experimental information about the magnitude of K_2 since these approximate solutions do not contain this parameter. We will first consider data which can be described in terms of the steady-state solution. This will be followed by a comparison of other experimental data with the transient solution.

A. 65°K thermal annealing

The isothermal annealing data presented in Sec. III B suggest that the steady-state solution in Eq. (13) is the appropriate approximation to consider for this case. For long annealing times, the data fit the empirical Eq. (3) which is of the same form as the solution given by Eq. (13). The parameter of interest is the rate constant K obtained from the

slope in Figs. 5 and 6 and found experimentally to be

$$K \approx 3\times 10^{10} e^{-(0.15\ \mathrm{eV})/kT}\ \mathrm{sec}^{-1}. \tag{15}$$

This value is to be compared with the calculated constant $2K_3V_0^2/i_0$ in Eq. (13), where K_3 can be calculated from Eq. (10).

To calculate K_3, we first observe that $P_v(-1) = P_v(0) = 0$ and that $P_v(-2) = 1$. These conditions are required from the experimental result that pulsed electric fields from 20 to 100 V/cm corresponding to electron temperatures in the range of 40 to 120 °K, tend to fill the double acceptors completely.[3] Therefore, this defect should also be filled thermally in the temperature range covered in the pulse isothermal annealing experiment.

After substituting the above probabilities into Eq. (10), we find that K_3 is given by

$$K_3 = P_I(+1)\sigma_{v(-2)} v_I. \tag{16}$$

If we assume that the capture cross section for capturing positive interstitials at the double negative vacancies is determined mainly by Coulomb attraction, then, calling the capture radius r_c,

$$\sigma_{v(-2)} = \pi r_c^2 = \pi(2e^2/\kappa kT)^2, \tag{17}$$

where r_c can be estimated from the expression

$$kT \approx |Z_I Z_v| e^2/\kappa r_c \tag{18}$$

and where Z_I and Z_v are charges in electronic units for the interstitial and vacancy respectively, $\kappa = 16$ is the relative dielectric constant of the crystal, and e is the electronic charge.

The interstitial velocity is given by[27,28]

$$v_I \approx (3kT/M)^{1/2} e^{-E_m/kT}, \tag{19}$$

where $(3kT/M)^{1/2}$ is the thermal velocity of a completely free interstitial, M is the germanium interstitial mass, and E_m is the interstitial migration energy. In all the calculations to follow in which v_I is needed, we will assume that $E_m = 0.005$ eV. This low migration energy agrees with the estimate made for the migration energy of the Si interstitial by Watkins[15] and also with the activation energy associated with radiation annealing of the 65 °K defects in germanium at near liquid-helium temperatures as measured by Hyatt and Koehler.[29]

The probability for thermal ionization of electrons from free interstitials is given by

$$P_I(+1) = \frac{I^+}{I^+ + I^0} = \frac{1}{1+\beta^{-1}e^{\gamma-\delta}} \approx \beta e^{\delta-\gamma}, \tag{20}$$

where $\delta = (E - E_c)/kT$, $\gamma = (\Phi - E_c)/kT$, β is the degeneracy factor for the free interstitial donor level, $E_c - E$ is the ionization energy of this level, and $E_c - \phi$ is the difference in energy between the bottom of the conduction band at E_c and the Fermi energy at ϕ. The last approximation in Eq. (20) can be justified as follows. If we assume that the donor character of the impurities involved in complexes is essentially the same as for the unoccupied donor impurities, then charge conservation and nondegeneracy imply that

$$n_0 = N_c e^{\gamma} = i_0 - 2V + (V - C)/(1+\beta^{-1}e^{\gamma-\delta}), \tag{21}$$

where n_0 is the exhaustion-range carrier concentration and is approximately equal to i_0 before irradiation. The last term in Eq. (21) is the positive free interstitial concentration $I^+ = P_I(+1)I = P_I(+1)(V-C)$. We have also used $V^{--} = P_v(-2)V = V$ since $P_v(-2) = 1$. The quantity N_c is the effective density of conduction band states and is defined as

$$N_c = 2(2\pi m_e^* kT/h^2)^{3/2} = 2.2\times 10^{15} T^{3/2}\ \mathrm{cm}^{-3},$$

where m_e^* is the electron effective mass and h is Planck's constant. From Eq. (21) it is apparent that e^{γ} is of the order of 10^{-5} since n_0 is of the order of 10^{13}–10^{14} cm^{-3} during the entire anneal. Also, $e^{-\delta}$ is of the order of 10^{12} for temperatures from 50 to 60 °K if we assume that $E_c - E = 0.15$ eV, the activation energy associated with the long time isothermal annealing. Therefore, $e^{\gamma-\delta}$ is of the order of 10^7 which is much larger than unity and justifies the last approximation in Eq. (20).

To obtain an expression for $P_I(+1)$ in terms of known quantities, we must now determine e^{γ}. From Eq. (21), and using the approximation that $e^{\gamma-\delta} \gg 1$,

$$e^{\gamma} = \frac{i_0 - 2V}{N_c} + \frac{V-C}{N_c}\beta e^{\delta-\gamma}.$$

But the last term in this equation is at least 10^5 times smaller than the first term because $e^{\delta-\gamma}$ is of the order of 10^{-5} while $V - C$ is of the same order as $i_0 - 2V$. Thus, $e^{-\gamma} = N_c/(i_0 - 2V) \approx N_c/i_0$ to the same approximation as was used in the steady model. Equation (20) now becomes

$$P_i(+1) \approx (N_c/i_0)e^{-(E_c-E)/kT}.$$

We can write immediately a expression for the effective annealing rate K, using Eq. (16) and the above equation, i.e.,

$$K = \frac{2K_3V_0^2}{i_0} \approx 2\beta N_c\left(\frac{V_0}{i_0}\right)^2 \sigma_{v(-2)} v_I e^{-(E_c-E)/kT}. \tag{22}$$

For the samples used, and assuming the vacancy to be a double acceptor, $(V_0/i_0)^2 = 1.75\times 10^{-2}$. Using this value, the last equation, Eqs. (17) and (19), the definition of N_c, and setting $\beta = 1$ and $E_c - E = 0.15$ eV, we find that $2K_3V_0^2/i_0 = 1.96\times 10^{10} \times e^{(-0.15\ \mathrm{eV})/kT}$ sec^{-1} which compares quite favorably with the experimental results in Eq. (15). Figure 8 shows a typical isothermal anneal at 56 °K in which the solid line on the figure is calculated from Eq. (22).

The initial vacancy concentration V_0 occurs in Eq. (22) only in the ratio V_0/i_0. In typical experi-

ments, this ratio is approximately constant for samples whose exhaustion range carrier concentration varies over several orders of magnitude. This is because irradiations are usually sufficiently long so as to produce a measurable change in the conductivity or carrier concentration. The total fluence, and hence V_0, is therefore more or less dependent on the impurity concentration i_0 for purposes of experimental convenience and sensitivity. This may explain why no strong dependence on the concentration of group-V impurities has been observed in the past.[3]

B. Optical annealing at 4.2°K

Arimura has obtained optical annealing data which have been difficult to fit into a close-pair model or a diffusion model.[7,22] When light from a glow-bar, filtered through a thick Ge filter to produce light of energy less than the band gap ($h\nu < E_g$), is allowed to illuminate a sample containing 65 °K defects, optically stimulated annealing of these defects is observed to occur at 4.2 °K.[7] We have analyzed these data and observe that the annealing kinetics are similar to the 65 °K thermal annealing kinetics and to the radiation annealing kinetics.[12] The data for long annealing times can be described by Eq. (3). This is illustrated in Fig. 9, where $1/f^2$ has been plotted versus the annealing time to obtain a linear plot. The steady-state approximation described by Eq. (13) is again appropriate.

The recovery due to optical annealing at 4.2 °K is at the expense of the 65 °K thermal recovery.[7] The filtered light has shifted the annealing some 50–60 °K lower in temperature. This extrinsic light must break up the impurity interstitial complexes at 4.2 °K in at least small numbers. We propose that the neutral interstitial is bound to the

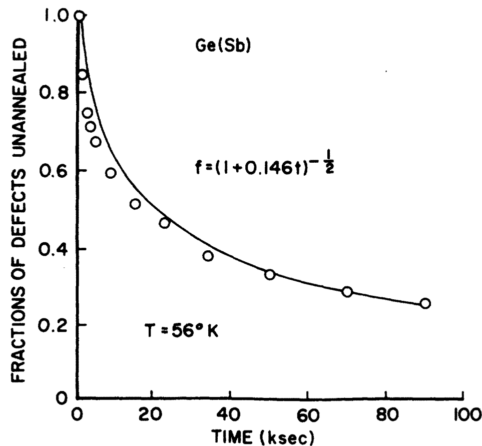

FIG. 8. Fit of the steady state approximation given by Eq. (13) to a pulse isothermal anneal at 56 °K using the calculated rate constant $2K_3V_0^2/i_0$.

group-V impurity atom by sharing an electron with the impurity as well as by an attractive strain field. By photoexciting this electron from the complex, the interstitial is aided in its escape by the Coulomb repulsion created between the ionized impurity and ionized interstitial.

The annealing rate at 4.2 °K is given by the slope in Fig. 9. From this figure we find that $K = 8\times10^{-4}$ sec^{-1}. Again, by comparing Eqs. (3) and (13), this experimental value should be identical to $2K_3V_0^2/i_0$, where K_3 is given by Eq. (10). From Arimura's data, $i_0 = 3\times10^{14}$ cm^{-3}, while $V_0 = 4.5\times10^{13}$ cm^{-3}. On the basis of photoconductivity measurements by Arimura,[22] the filtered light used to stimulate annealing causes single ionization of all the double acceptors as well as a partial double ionization of these defects. Therefore, $P_v(-2) = 0$ and from Eq. (10),

$$K_3 = P_I(+1)P_v(-1)\sigma_{v(-1)}v_I , \tag{23}$$

where v_I is calculated by Eq. (19) using $T = 4.2$ °K and $E_m = 0.005$ eV. The capture cross section $\sigma_{v(-1)}$ is similar to $\sigma_{v(-2)}$ in Eqs. (17) and (18) except that now, $Z_v = -1$. Therefore, we find that

$$\sigma_{v(-1)} = \pi(e^2/\kappa kT)^2 . \tag{24}$$

We proceed now with a calculation of $P_I(+1)P_v(-1)$. In the presence of filtered extrinsic light, electrons are excited from and recaptured at vacancies and interstitials until an electronic steady state occurs. After this steady state is reached ($dn/dt = 0$), assuming detailed balance and also assuming that the thermal generation rates at 4.2 °K are negligible compared to the optical generation rates

$$I^+/I_0 = g_{I0}/[nv_e\sigma_e(+)]$$

and

$$V^-/V^0 = nv_e\sigma_e(0)/g_{v^-} ,$$

where g_{I0} is the rate at which electrons are generated from neutral interstitials, g_{v^-} the rate electrons are generated from negative vacancies, v_e the electronic thermal velocity given by $v_e = (3kT/m_e^*)^{1/2}$, $n = n_0 + \Delta n$ is the steady-state electron concentration in the conduction band, and $\sigma_e(+)$ and $\sigma_e(0)$ are the capture cross sections for capturing electrons at a positive interstitial or a neutral vacancy. If Δn, the excess electron concentration, is not too large compared to n_0, the exhaustion range electron concentration, then $I^+/I^0 \approx P_I(+1)$ and $V^-/V^0 \approx P_v(-1)$. Assuming that g_{I0} is not too different from g_{v^-}, then

$$P_I(+1)P_v(-1) \approx \sigma_e(0)/\sigma_e(+) . \tag{25}$$

The calculation of K_3 in Eq. (23) can be made at once if the ratio of these electronic cross sections is known. These capture cross sections have not been measured experimentally, however, these

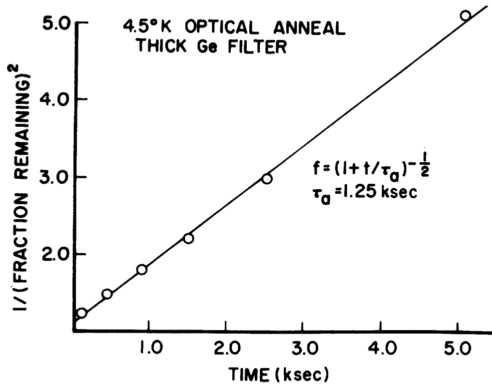

FIG. 9. Thick-filter optical annealing at 4.5 °K illustrating the long-time approximation $f \propto t^{-1/2}$. Original data are from Refs. 7 and 12 with permission of the authors.

values can be estimated from data given by Lax[30] for capture cross sections at other types of flaws in various charge states. We will assume the following representative values at 30 °K to be

$$\sigma_e(-)=\sigma_h(+)=10^{-19}\ \text{cm}^2,$$
$$\sigma_e(0)=\sigma_h(0)=10^{-16}\ \text{cm}^2, \qquad (26)$$
$$\sigma_e(+)=\sigma_h(-)=10^{-13}\ \text{cm}^2,$$

where $\sigma_e(q)$ is the electron capture cross section for a defect of charge q while $\sigma_h(q)$ is the corresponding hole capture cross section. The temperature dependence of $\sigma_e(+)$ can be estimated since attractive Coulomb forces are involved in the capture process. By analogy with Eq. (24), $\sigma_e(+) \propto (kT)^{-2}$. Therefore, $\sigma_e(+) \approx 5\times10^{-12}$ cm^2 and $\sigma_e(0) \approx 10^{-16}$ cm^2 at 4.2 °K. Using these cross sections, the values of i_0 and V_0 given at the beginning of this subsection, and calculating $\sigma_{v(-1)}v_I$ from Eqs. (19) and (24), we obtain $2K_3V_0^2/i_0 = 13.8\times10^{-4}$ sec^{-1}. This is reasonably close to the experimental value, $K=8\times10^{-4}$ sec^{-1}, obtained from Fig. 9.

C. Radiation annealing at 7°K

The rate constant for radiation annealing was determined in Sec. III C to be $K=11.2\times10^{-4}$ sec^{-1}. Since the steady-state approximation fits the data, we again calculate the effective rate $2K_3V_0^2/i_0$. As was the case in Sec. V B, $V_0=4.5\times10^{13}$ cm^{-3} and $i_0=3\times10^{14}$ cm^{-3}. The calculation of K_3 is similar to the calculation of this quantity in Sec. V B except that in this case the electron beam heats the sample to a temperature of 7 °K. This heating increases the free interstitial velocity considerably since the migration energy is taken to be $E_m=0.005$ eV. The probability terms in Eq. (10) must also be recalculated because the 500-keV-electron beam produces many electron-hole pairs which affect the defect occupation probabilities.

We expect that, in the presence of large numbers of electrons and holes, the interstitials and vacancies will have a large probability of being neutral. Let $t_e=(nv_e\sigma_e)^{-1}$ be the time for a particular defect to capture an electron and $t_h=(pv_h\sigma_h)^{-1}$ be the time for hole capture at this same defect where n and p are the steady-state concentrations of free electrons and holes, v_e and v_h are the electron and hole thermal velocities, and σ_e and σ_h are the electron and hole capture cross sections at the defect. If $P(h)$ is the probability for occupation of the defect by a hole and $P(e)$ the probability of occupation by an electron, then

$$P(e)=t_h/(t_e+t_h)$$
and $\qquad (27)$
$$P(h)=t_e/(t_e+t_h).$$

The probability that a vacancy will capture two electrons is very small since once the first electron is captured the time to capture a hole is 10^6 times as fast as the time to capture a second electron. We can therefore take $P_v(-2)=0$. From Eq. (27) then,

$$P_I(+1)=[1+nv_e\sigma_e(+)/pv_h\sigma_h(0)]^{-1}$$
and $\qquad (28)$
$$P_v(-1)=[1+pv_h\sigma_h(-1)/nv_e\sigma_e(0)]^{-1}.$$

But since $v_e \approx v_h$ and $n\approx p$, then

$$P_v(-1)P_I(+1)\approx \sigma_e(0)\sigma_h(0)/\sigma_e(+)\sigma_h(-). \qquad (29)$$

Using Eq. (26), $\sigma_e(0)=\sigma_h(0)=10^{-16}$ cm^2. Also $\sigma_h(-) = \sigma_e(+) = (\frac{30}{7})^2\times10^{-13}$ cm^2 where the temperature dependence of these cross sections is estimated as before. Using Eqs. (19) and (24) to calculate $\sigma_{v(-)}v_I$ at 7 °K, and Eqs. (29) and (23), then $2K_3V_0^2/i_0 = 8.5\times10^{-4}$ sec^{-1} as compared to the experimental value of $K=11.2\times10^{-4}$ sec^{-1}.

D. Optical annealing at 30°K

Arimura has reported that very little optical annealing is observed at 4.2 °K when monochromatic light of energy greater than the band gap ($h\nu > E_g$) illuminated a sample containing 65 °K defects.[7] Using the same analysis as was used to calculate the radiation annealing rate, but at a temperature of 4.2 °K, the greater than band gap light optical annealing rate at this temperature is found to be 1.5×10^{-6} sec^{-1}. This rate is too slow to be observed conveniently since 10^6 sec are required to observe a 30% decrease in the fraction of defects remaining. The difference between the intrinsic light and the radiation annealing can be attributed entirely to the difference in temperature in the two experiments. Since this temperature difference most strongly affects the interstitial migration velocity, $v_I=(3kT/M)^{1/2}e^{-E_m/kT}$, a comparison of

these two experiments has led to the determination of the interstitial migration energy $E_m = 0.005$ eV. An activation energy of this size has recently been observed by Hyatt and Koehler[29] from a study of the temperature dependence of the radiation annealing near 4.2 °K.

The annealing rates for greater than band-gap illumination and radiation annealing increase rapidly in the temperature range of 30 °K.[7,31] Figure 10 shows isothermal annealing data taken at 30 °K for the annealing of 65 °K defects by greater than band-gap monochromatic light.[22] We have been able to obtain a reasonable fit to these data using the transient solution given by Eq. (14). This is illustrated in Fig. 10 by the solid line which is calculated from Eq. (14) using the empirically determined values for the two parameters, $u_0 = 1.0$ and $K_1 = \frac{1}{60}$ sec^{-1}. We now proceed with a calculation of these two parameters.

Arimura has estimated Δp, the excess hole concentration generated by the intrinsic light in this experiment, from the relation $\Delta p = \alpha I_0 \tau_p$, where $\alpha = 5$ cm^{-1} is the optical absorption coefficient for

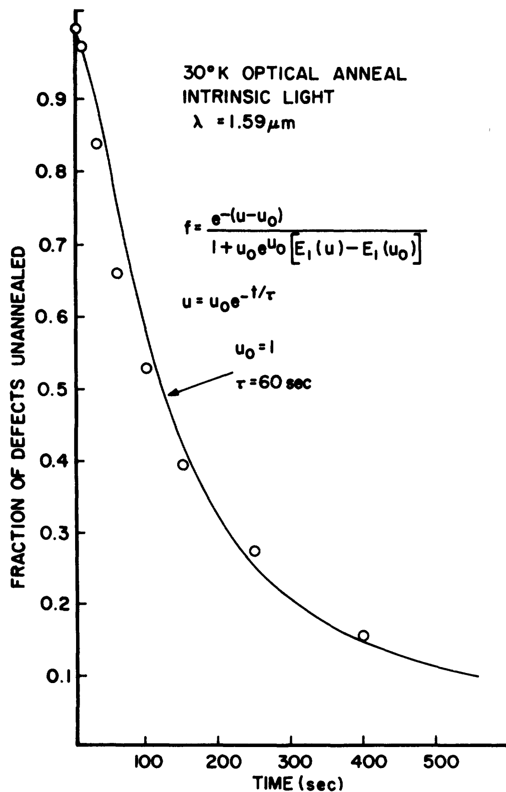

FIG. 10. Fit of the transient approximation given by Eq. (14) to monochromatic light ($h\nu > E_g$) optical annealing data obtained from Ref. 22. Data used with permission of the author. The values $u_0 = 1$ and $\tau = 60$ sec were determined empirically.

the wavelength of light used, τ_p is the minority carrier lifetime at 30 °K which is taken to be about 10^{-5} sec,[22] and $I_0 = 10^{14}$ photons/cm^2 sec is the photon intensity as estimated by Arimura. From these values, the free hole concentration $p \approx \Delta p = 5 \times 10^9$ cm^{-3}. The number of electrons thermally ionized from the donor levels is about 60% of the exhaustion range concentration in the sample used in this experiment and is much larger than the excess electrons generated by the light. Therefore, $n = 2 \times 10^{14}$ cm^{-3}. Using these values for n and p and Eq. (28), we find that $P_v(-1) \approx 1$ while $P_I(+1) = 2.5 \times 10^{-8}$. The rapid rise in both the radiation annealing rate and the optical annealing rate can be attributed to the rapid rate at which vacancies become negative in this temperature range due to thermal ionization of the donor levels. This enhances the probability for the vacancies to capture positive interstitials.

At 4.2 °K, the defect complex is comprised of a neutral interstitial and a neutral group-V impurity. Therefore, the complex is probably neutral. If we assume that complexes are thermally ionized singly in the same temperature range as the group-V impurities, then a double ionization will occur in the 30 °K temperature range primarily by hole capture at singly ionized complexes. This should create a Coulomb repulsion between the interstitial and the group-V impurity which will break up the complex. The rate of break up K_1 is determined by the rate of hole capture. Therefore, $K_1 = 1/t_h = p v_h \sigma_h(+)$. Using $p = 5 \times 10^9$ cm^{-3}, as estimated in the last paragraph, and $\sigma_h(+) = 10^{-19}$ cm^2, and calculating v_h from $v_h = (3kT/m_h^*)^{1/2}$, where m_h^* is the hole effective mass, we calculate that $K_1 = 2.5 \times 10^{-2}$ sec^{-1} in good agreement with the experimental value of $K_1 = \frac{1}{60}$ sec^{-1} = 1.67×10^{-2} sec^{-1}.

We now have all the data required to calculate $u_0 = K_3 V_0 / K_1$. Using Eq. (10) and setting $P_v(-2) = 0$ for reasons given in Sec. V C, then

$$u_0 = \sigma_{v(-1)} v_I P_v(-1) P_I(+1) V_0 / K_1 .$$

Calculating $\sigma_{v(-1)} v_I$ as before and using again $V_0 = 4.5 \times 10^{13}$ cm^{-3}, the calculated value of u_0 is 1.7 as compared to the experimental value of 1.0.

VI. ANNEALING AT 35°K

The analysis in previous sections has been restricted to the case of lightly irradiated and lightly doped n-type Ge. This approach was taken because most of the experimental data which depend upon the defects's charge states have been obtained under these conditions.[3,5–7,11,12,22,29] All the experimental data presented in this paper also belong to this category. Furthermore, optical annealing of degenerate n-type Ge damaged at 10 °K has not been reported to our knowledge. Radiation annealing has, however, been observed at 10 °K,[1–3,31,32]

suggesting that the defects's charge states are still an important consideration in the degenerate case. A discussion of radiation annealing caused by ionization in degenerate n-type Ge has been presented by MacKay and Klontz in terms of a charge-state-dependent impurity trapping model.[13]

The most notable difference in the response of degenerate and nondegenerate n-type Ge to low-temperature electron irradiation is the appearance of a thermal annealing stage at 35 °K in degenerate material and the lack of this stage in nondegenerate material.[3,32,33] Several models for the 35 °K annealing stage have been proposed, however, conflicting experimental results, due presumably to different experimental conditions,[1,2,4,10,13,31-36] make interpretation of the data for this stage rather speculative at this time. Therefore, we will not attempt to present here a quantitative model for this annealing stage. Rather, we will discuss qualitatively how this stage can be accommodated within the framework of the model presented in the previous sections.

The principal experimental results which have been reported for the 35 °K annealing stage are as follows:

1. This stage has not been observed in material in which the group-V donor concentration is less than some as yet undetermined critical value which is approximately 10^{16}–10^{17} cm^{-3}.[3,36]

2. In samples doped with approximately 10^{17} Sb/cm^3, a critical fluence for the production of 35 °K defects has been observed which is approximately 5×10^{16} e/cm^2 for a 1.1-MeV irradiation from a pulsed electron source.[2,13]

3. In samples doped with 10^{18} As/cm^3, the production of these defects, using a 1-MeV dc electron beam, is more efficient than in the previous case.[10,35,36] This could be due to a lowering of the critical fluence for production of 35 °K defects because of a concentration dependence, an impurity type effect, pulsed beam versus dc beam ionization effects, some combination of these reasons or other unknown experimental differences such as the degree of compensation in the samples used in these experiments.[37,38]

4. Radiation annealing of 65 °K defects, after a thermal anneal to remove 35 °K defects, produces additional 35 °K defects.[31,35]

5. Thermal annealing kinetics for the 35 °K stage have usually been reported as first order for, in some cases, greater than 80% of the recovery.[1,2,31-33] In contrast, Bourgoin and Mollot report the annealing kinetics to be third order near the end of the anneal.[10,36] Activation energies for this stage have been reported to be as low as 0.017 eV[33] and as high as 0.07 eV.[31]

6. A large stored-energy release accompanies the 35 °K recovery suggesting that vacancy-interstitial recombination occurs in this stage as well as in the 65 °K stage.[4,5]

7. Models for the 35 °K annealing have been proposed suggesting that this stage is caused by the annealing of the closest of close pairs of vacancies and interstitials,[1] by the annihilation of defects converted by irradiation from permanent defects[2] (those defects not annealing at 35 or 65 °K), that the 35 °K defects are produced directly as primary defects when permanent defects are present,[35] that 65 °K defects are converted into 35 °K defects after prolonged irradiation,[35] or that this stage results from the recombination of impurity interstitials with vacancies.[10,36]

8. In conflict with the dependence of the 35 °K defect production rate on permanent defect concentration reported by Klontz and MacKay[2] for samples doped with 10^{17} Sb/cm^3, Bourgoin and Mollot[10] report no observed production rate dependence on the permanent defect concentration for samples doped with 7×10^{17} As/cm^3 for fluences greater than 5×10^{16} e/cm^2.

9. At high impurity concentrations and higher electron energies, the production rate for 35 °K defects increases with increasing group-V impurity concentration in As-doped samples.[10]

10. The production of 35 °K defects increases with increasing electron energy up to 900 keV, but decreases at higher energies in samples highly doped with As.[35]

Although there exists considerable disagreement as to the interpretation of these experimental results, the 35 °K annealing stage is generally believed to be the result of annihilation of either self-interstitials[4] or impurity interstitials[10,36] at vacancy sites. These interpretations are in agreement with the stored energy release during annealing for this stage.[4,5]

The observation that 35 °K annealing occurs only in degenerate material can be interpreted in terms of a Fermi-level dependence or donor-impurity concentration dependence. Bourgoin and Mollot have demonstrated, however, that 35 °K defect production is the same in two samples doped with the same As-impurity concentration but different compensations, and that samples of different As-impurity concentration have different 35 °K defect production rates.[10] We therefore conclude that the group-V impurity concentration is more important than Fermi level position in determining the production of 35 °K defects.

Since the production of 35 °K defects has been shown to be at the expense of defect concentrations created at lower fluences,[2,34,35] it has been suggested by MacKay and Klontz that prolonged irradiation modifies primary defects into 35 °K defects.[2] From a slightly different point of view, these defects can be thought of as arising from defect in-

teractions which become more important after prolonged irradiation due to an increase in defect concentration.

In terms of the model presented in previous sections, irradiation at 1 MeV produces isolated vacancies and interstitial-group-V impurity complexes in nearly equal concentrations which are randomly distributed throughout the crystal. In lightly doped crystals, the vacancy interstitial separation distance is large compared to the capture radius for interstitials at vacancy sites for all measurable defect concentrations, i.e., concentrations of vacancies less than the group-V donor impurity concentration. As the impurity concentration is increased, however, the probability that an interstitial will be trapped at an impurity site which falls within a vacancy capture radius for interstitials (which is a function of both the vacancy and the interstitial charge states) must necessarily increase with both increasing impurity concentration and increasing vacancy concentration which is proportional to fluence. If no Coulomb attraction exists between the vacancy and interstitial, then this capture radius is of the order of a few lattice constants and is determined primarily by lattice strain. However, with a Coulomb attraction between the vacancy and interstitial, the capture radius at a vacancy site for interstitials of the opposite charge state is, from Eq. (18), approximately 100–300 Å at 35 °K depending on electron screening of the Coulomb potential. Therefore, those interstitials which are closer to vacancies than this radius should spontaneously annihilate provided that the defects can be forced into suitable charge states either thermally or by other means.

The rate of annihilation at 35 °K will be governed, therefore, by the capture of holes at interstitials, assuming that the vacancies are all negative. Approximately first-order annealing kinetics with the rate governed by hole capture are expected for this model. The fraction of defects which annihilate, however, is expected to be a function of both the group-V impurity concentration and the vacancy concentration since both of these concentrations determine the mean vacancy-interstitial separation distance.

This model is capable of explaining many of the seemingly contradictory experimental data previously discussed. Assuming that the impurities, and hence the interstitials, are distributed more or less randomly with respect to the vacancies, and using a reasonable distribution function for the vacancy interstitial separation distance[39]; it is possible to show that 35 °K defects are not expected to be observed until the group-V impurity concentration is greater than 10^{16} cm^{-3}.[40] Also, this model predicts that a critical fluence of somewhat greater than 10^{16} 1-MeV electrons/cm^2 is required to produce 35 °K defects in a sample doped to an impurity concentration of 1×10^{17} cm^{-3} in agreement with experiment.[2] Furthermore, the calculated fraction of total defects annealing in the 35 °K stage is also in reasonable agreement with experiment. For more highly doped material (10^{18} impurities/cm^3), it can be shown that some interstitials fall within the vacancy capture radius after very small defect concentrations have been produced in agreement with the results of Bourgoin and Mollot.[10]

A consideration of the discussion of radiation annealing in Sec. V suggests how 35 °K defects can be formed by low-energy electron irradiation following a thermal anneal which removes all of these defects. During the radiation anneal, interstitials are being released and retrapped at complexes at a rate which is much larger than the vacancy interstitial recombination rate. This conclusion is drawn from the model in the previous section and from the experimental fact that the radiation annealing kinetics are approximately third order. Since relatively small fractions of these defects are simultaneously in suitable charge states for annihilation during the radiation annealing process, it is expected that the vacancy-interstitial distribution would tend to become random during radiation annealing. Therefore, a fraction of the remaining interstitials would again fall within the vacancy capture radius forming new 35 °K defects. It is expected that the fraction of defects converted to 35 °K defects on subsequent cycles of this process should decrease as the total number of defects decreases. This effect has been observed by DeAngelis and Penczer.[34]

The nature of the spread in thermal activation energies associated with the 35 °K annealing stage is not obvious from the model presented in this section. Isothermal annealing data under different impurity and defect concentrations have not been reported. Several factors may contribute to the total binding energy of impurity-interstitial complexes. The relative importance of these contributions for different concentrations may possibly account for the observed spread in activation energies. Since radiation annealing of 35 °K defects can occur near liquid-helium temperatures, it is likely that a large part of the activation energy is electronic in nature. The Coulomb repulsion between an electron trapped at a vacancy and an electron trapped in a complex closer to this vacancy than 100 Å is larger than 0.02 eV. For much closer spacings, this repulsion energy is correspondingly larger. This effect tends to lower the total complex binding energy. Also, impurity level thermal ionization becomes significant in the same temperature range in which this annealing is observed. A loss of electrons thermally from impurities involved in complexes would further reduce

the total binding energy of these complexes.

Another factor leading to thermal activation in irradiated degenerate semiconductors is low-temperature carrier hopping. In previous sections, we have proposed that hole capture by complexes is an important mechanism for dissociation. In highly compensated degenerate semiconductors, conduction through the impurity band occurs by the hopping mechanism which is thermally activated.[41-43] Experimental data by Fritzsche[44] on Sb-doped Ge indicate that concentrations of 1×10^{17} Sb/cm^3 just place this material into the metallic conduction state. Any compensation produced by irradiation in samples doped with this concentration is expected to produce thermally activated conduction (see Fig. 4 in Ref. 44). Furthermore, in highly degenerate semiconductors which are also highly compensated, Shklovskii and Efros[45] have shown that the electrons are very inhomogeneously distributed in space. As a result, the electrons form metallic drops at low temperature which are separated from each other by very large potential barriers. The conductivity is therefore thermally activated over a large temperature range with activation energies as high as 0.1 eV in some cases.[45] It is possible that a complete understanding of the 35 °K defect will ultimately depend upon a thorough explanation of the intermediate conduction process described in Refs. 41–45.

The production of permanent defects, which increases rapidly with electron irradiation energy above 900 keV, causes a type of carrier compensation which does not anneal at 35 or 65 °K.[3] These defects can affect the 35 °K annealing by introducing additional defect-defect interactions as well as producing further modification of the conduction process through compensation. Other defects which can conceivably occur in significant concentrations after prolonged irradiation include di-interstitials, divacancies, and di-interstitial impurity complexes. It is not possible, on the basis of present experiments, to completely exclude any of these defect configurations from the 35 °K annealing at this time.

VII. DISCUSSION OF PREVIOUS MODELS

Due to a lack of microscopic experimental information about the defects produced by irradiation in Ge, very few conclusive defect identifications have been made in this material. This has resulted in considerable revision of previous models proposed to explain the observed annealing stages as new experimental data have become available. The model which has been presented here is no exception to this. We have attempted in this paper to fully develop the concepts of "interstitial trapping" and "Coulomb capture cross section" to a point where quantitative contact with experimental data is possible. The results, which are summarized in Table II, have been encouraging. It should be emphasized, however, that this model may not be unique in its ability to yield order of magnitude values for the experimental annealing parameters measured thus far. It is hoped that the results which have been presented here will serve as a stimulus to further experimentation and that other proposed models will be developed to the stage where a more quantitative comparison with experiment is possible. It is appropriate, therefore, to briefly discuss other models which have been proposed in the literature as an aid to future development in this area.

The models which have been proposed fall generally into three broad areas and can be classified in terms of the relative positions hypothesized for the vacancy and interstitial immediately after irradiation. In addition to the interstitial trapping model presented in Sec. V, other models for the low temperature annealing have included several close-pair models as well as a correlated diffusion annealing model. A comparison of the currently popular models is presented in Ref. 13.

Close-pair models have been proposed many times in order to explain the low-temperature annealing in n-type Ge.[1-4,7,22,31-35] The assumption made in these models is that a very high degree of correlation exists between interstitials and their parent vacancies, due to their proximity, so that during recovery, each interstitial annihilates the vacancy from which it originated. Electrons captured in the close-pair stabilize the defect structure as a whole and the observed charge dependent shift of annealing temperature is due to a loss of stabilizing electrons. The obvious advantage of close-pair models is the ease of explaining the high percentage recovery observed for thermal annealing at 65 °K and radiation annealing at 10 °K. Close-pair models do not, at present, yield the correct annealing kinetics in any obvious way,[6] account for the dependence of the 65 °K annealing on impurity type, or account for the dependence of 35 °K annealing on impurity concentration.[10]

It has been suggested that the Fermi energy accounts for a part of the measured activation energy of the 65 °K annealing.[8,9,46,47] It has also been suggested that the impurity type dependence for this stage could be due to a difference in ionization energy of the group-V impurities as reflected in the position of the Fermi level.[10] By a suitable combination of these suggestions, it is possible to qualitatively account for the dependence of 65 °K annealing on the type of impurity within the framework of a close-pair model. If the effect of defect concentration on Fermi-level position is also included, as we have done for the trapping model in Sec. V, then perhaps the observed annealing kinetics can also be explained.

TABLE II. Comparison of calculated annealing parameters with experimentally determined values.

Type of annealing	Parameter	Calculated value	Experimental value
Thermal annealing at 65 °K	Effective rate constant	$1.96\times 10^{10}\ e^{-(0.15\,\mathrm{eV})/kT}\ \mathrm{sec}^{-1}$	$3\times 10^{10}\ e^{-(0.15\,\mathrm{eV})/kT}\ \mathrm{sec}^{-1}$
Filtered light optical Annealing at 4.2 °K ($h\nu < E_g$)	Effective rate constant	$13.8\times 10^{-4}\ \mathrm{sec}^{-1}$	$8.0\times 10^{-4}\ \mathrm{sec}^{-1}$
Radiation annealing at 7 °K	Effective rate constant	$8.5\times 10^{-4}\ \mathrm{sec}^{-1}$	$11.2\times 10^{-4}\ \mathrm{sec}^{-1}$
Monochromatic light optical annealing at 4.2 °K ($h\nu > E_g$)	Effective rate constant	$1.5\times 10^{-6}\ \mathrm{sec}^{-1}$	$\ll 10^{-3}\ \mathrm{sec}^{-1}$
Monochromatic light optical annealing at 30 °K ($h\nu > E_g$)	$u_0 = K_3V_0/K_1$ K_1	1.7 $2.5\times 10^{-2}\ \mathrm{sec}^{-1}$	1.0 $1.67\times 10^{-2}\ \mathrm{sec}^{-1}$

The impurity dependence observed for radiation annealing and the dependence of 35 °K annealing on impurity concentration are more difficult to explain, however. During radiation annealing, large numbers of electron-hole pairs are generated which must be described in terms of quasi Fermi levels which are much deeper in the gap than the equilibrium Fermi level in nondegenerate material. Neither the impurity dependence nor the annealing kinetics are obvious in this case. Presumably the 35 °K annealing in degenerate material would have to be described in terms of interstitial migration over large distances as suggested by Bourgoin and Mollot.[10,36] It may not be possible to resolve this long-range migration with a close-pair model.

In the correlated diffusion models, the mean separation distance between vacancies and interstitials is assumed to be greater than a few lattice constants. A high degree of correlation is proposed, however, in order to account for the high percentage recovery at 65 °K. Lower-temperature annealing stages are attributed to lower interstitial migration energies produced by changes in defect charge state induced by various external stimuli.[5,6,10,11,29] The annealing kinetics are described by the diffusion theory of Waite[26] using only those terms which represent correlated recovery. Hyatt and Koehler[29] have shown that the isothermal annealing kinetics at a single temperature (66.3 °K) can be fit with this model quite well. No one has demonstrated, however, that the same interstitial distribution function can be used to fit all the available isothermal data near 65 °K. Hyatt and Koehler have also pointed out the importance of the Coulomb capture radius at low temperatures.[29] Using this concept, however, they arrive at abnormally low interstitial diffusion coefficients and can not account for these numbers in terms of random walk through the lattice either for the radiation annealing case or the thermal annealing at 65 °K. MacKay and Klontz[13] have shown that no high degree of correlation is expected to exist in lightly doped material for interstitials in the 0 or ±1 charge states after irradiation sufficient to produce measurable concentrations of defects. The impurity dependence is explained as a Fermi-level effect except for the 35 °K annealing for which a different mechanism is proposed.[10]

The correlated diffusion of interstitials toward sinks in the presence of an interaction potential which is dependent on distance, due either to Coulomb forces or strain fields, has not been considered theoretically in the Waite model. The Waite theory applies only to the case of particles exerting short-range chemical forces which are independent of position.[26] In the radiation annealing case, the defects's charge states are changing in times of the order of the free carrier lifetimes. The potential term which must be added to each probability diffusion equation in Waite's theory is in general both position and time dependent. There is no theoretical justification for discarding the uncorrelated terms, or assuming that the third order annealing kinetics will result under these conditions. It should also be pointed out that the optical annealing at 30 °K in the presence of greater-than-band-gap light is essentially first order and is more readily fit by our transient approximation than by a correlated diffusion theory.

A further difficulty arises in explaining the 35 °K annealing in terms of a diffusion model in the case of degenerate Ge.[13] Bourgoin and Mollot[10] introduce a completely different model for this stage. They have proposed that the 35 °K annealing stage is the result of group-V impurity interstitial annihilation at vacancy sites. They propose that during irradiation the Ge interstitials replace group-V impurities in concentrations large enough

to allow for the observed 35 °K recovery. For this to be so, the Ge interstitial must move distances larger than those calculated by Hyatt and Koehler.[29] It is not clear how the correlated distribution of Ge interstitials, which Bourgoin and Mollot[10] also advocate, is maintained under these conditions. The shape of the distribution function must obviously be distorted which will result in a different isothermal annealing behavior at 65 °K.

Perhaps further theoretical analysis will overcome some of these difficulties. We suggest that the concept of a Coulomb capture radius applied to the diffusion models may offer a more quantitative comparison with experiment. It is possible that the Coulomb potential can be introduced into Waite's theory only as an alteration of the capture radius around the vacancy. The problem of the oscillating charge states could be treated, perhaps, as a probability for occupation calculation which would then involve the defects's carrier capture cross sections as we have done in previous sections.

VIII. SUMMARY AND CONCLUSIONS

We have observed experimentally that the annealing rate of the 65 °K stage in irradiated n-type Ge depends on the type of group-V impurity used to dope the sample. The radiation annealing rate of these same defects at 7 °K is also sensitive to the type of doping impurity. Using this observed impurity dependence as a basis, and proposing that long range interstitial migration occurs in Ge near liquid-He temperatures, we have constructed a model which yields the observed annealing kinetics for the thermal annealing at 65 °K, the radiation and optical annealing near liquid-He temperature, and the greater than band-gap monochromatic light optical annealing at 30 °K. The charge states of the defects play a central role in this model. This model provides a means of calculating most of the annealing parameters which have been observed to date. These results are summarized in Table II.

We conclude that the 65 °K annealing stage, as well as the lower temperature annealing stages, produced as a result of external stimulation of various types, are the result of positive-interstitial negative-vacancy annihilation. The probability that these defects are in suitable charge states for Coulomb assisted annihilation directly affects the annealing rate. We have proposed that during irradiation most of the interstitials become trapped by group-V impurities to form defect complexes. The annealing process is then initiated by the release of these interstitials from the complexes.

Two types of annealing kinetics are possible depending on the amount of interstitial retrapping which occurs during the anneal. If the retrapping is large, then third-order kinetics dominate the annealing. This situation apparently exists for the majority of annealing experiments performed thus far. When interstitials are released from the complexes at a rate which is too rapid for a quasi-steady-stage between interstitial release and retrapping to become established, then the character of the annealing is more adequately described by the transient approximation given by Eq. (14). This situation occurs for monochromatic light optical annealing at 30 °K and probably also for 30 °K filtered light optical and radiation annealing, however no isothermal data exist with which to compare the model for these latter two cases.

The dependence of the annealing rate on impurity type has been observed to saturate for longer annealing times both in the radiation annealing experiment and the thermal annealing experiment. The annealing in both experiments is governed by the constant K_3 over an appreciable fraction of the recovery. This constant is expected to be independent of doping impurity type and accounts for the saturation of this impurity dependence. We expect the rate constant K_1 and possibly K_2 to depend on the type of impurity. The transient approximation, which is valid for early annealing times, predicts then that the impurity dependence should be most evident near the beginning of the anneal. Only during this transient does K_1, the impurity dependent rate constant, play an appreciable role in determining the over-all annealing rate.

The model presented here was based on the point of view that the behavior of vacancies and interstitials in both Si and Ge should in many ways be similar. We have obtained indirect evidence that the interstitial migration energy in these two materials is of similar magnitude. Whan[48] has presented data which suggest that vacancy migration occurs in Ge in the same temperature range as in Si. The formation of the vacancy-oxygen complex or A center occurs in the same temperature range in both materials.[48] All these experiments support the view that the effects of radiation on similar semiconductors may not be as diverse as has been suggested in the past.

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†The model presented in this paper and data of Figs. 4,

7, and 9 have been qualitatively discussed previously by J. M. Meese and J. W. MacKay at the International Radiation Damage in Semiconductors Conference, Albany, New York, 1970 (see Ref. 12).

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