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Effects of Low-Temperature Electron Irradiation on the Electrical Properties of Undoped GaSb*

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Undoped GaSb was irradiated with 1.0-MeV electrons near liquid-helium temperature and at ≈80°K. The effect on the Hall coefficient and the electrical resistivity was measured between 15 and 300°K. "Impurity" conduction, resulting from radiation-produced defects, was observed at low temperatures. At higher temperatures, where the normal conduction mechanism is predominant, the experimental data are consistent with a model characterized by radiation-produced acceptors with levels 0.023 eV above the top of the valence band and completely ionized radiation-produced donors. Isochronal and isothermal annealing studies were performed in the temperature range 15 to 440°K. No recovery was observed below 110°K. Major recovery stages were found near 122, 163, 203, and 365°K. Their activation energies were measured as 0.31 ± 0.02, 0.48 ± 0.03, 0.57 ± 0.03, and 1.0 ± 0.1 eV, respectively. The recovery near 122°K obeyed first-order kinetics. No simple recovery kinetics were found for the other stages.

I. INTRODUCTION

THE elements Al, Ga, In, and P, As, Sb are the components from which those III-V compound semiconductors are formed which crystallize in the zinc blende lattice under the influence of similar binding forces. Of the nine possible compounds only InSb has been investigated extensively with respect to radiation damage. It has been shown that in this material most of the radiation-induced damage recovers below room temperature.[1] Information on radiation effects in other III-V compounds is scarce and in most cases is based on irradiation at room temperature.[2] In the present work, undoped GaSb was irradiated with 1-MeV electrons at low temperatures. Bombardment with 1-MeV electrons results in energy transfers to the Ga and Sb atoms which are small enough to make multiple displacements rare events. Irradiations of GaSb have been reported with reactor neutrons at 140°K and at room temperature,[3] with 12-MeV deuterons at liquid-nitrogen temperature,[4] and with 4.5-MeV electrons at room temperature.[5] In all cases the average energy of a recoil atom is substantially larger than the threshold energy for displacement whose value can be expected to be not higher than 15 eV. Therefore, it is likely that the effects observed after these irradiations are influenced by the presence of more complicated defects created by high-energy recoil atoms.

In this work the temperature dependence of the resistivity and the Hall coefficient in the temperature range 15–300°K was measured after various irradiation doses up to 2×10^{17} electrons cm^{-2} and various annealing treatments. Some irradiations were performed near liquid-helium temperature; however, the majority of the irradiations were performed near 80°K. Both isochronal and isothermal annealing studies were performed, and the activation energies of the major recovery processes were determined.

An effort was made to extract information about the electrical nature of the radiation-produced defects from the experimental data. It was believed however, that it would be premature to attempt identification of the electrically characterized defects with particular point-defect configurations such as Ga and/or Sb interstitials and /or vacancies.

The experimental procedure is described in Sec. II. A characterization of the unirradiated samples is given in Sec. IIIA. Results concerning the dose and temperature dependence of the Hall coefficient and the Hall mobility of irradiated samples are presented and discussed in Sec. IIIB. The recovery of the radiation-induced changes is described and discussed in Sec. IIIC. The main results, and the conclusions derived from them, are summarized in Sec. IV.

II. EXPERIMENTAL PROCEDURES

The GaSb used in the present work was purchased from Bell and Howell Research Laboratories, Pasadena, California in the form of 0.09- to 0.13-mm-thick single-crystal wafers with the ⟨111⟩ axis normal to the large areas. Bridge-shaped samples were cut from these wafers using a sandblasting technique. The samples were soldered with 60/40 solder to a copper pedestal which had been silver soldered to a 5-mm-thick copper plate of 25-mm diameter (Fig. 1). This base plate had a 6-mm×12-mm window, so that the electron beam would not be stopped in the plate and increase its temperature during the irradiation. A sapphire rod was mounted on the base plate which provided tie points for the electrical leads near the sample. One-mil copper leads were attached to the sample with 60/40 solder, using a non-corrosive organic flux. Good Ohmic contacts were ob-

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[†] Work supported by Division of Research, Metallurgy and Materials Programs, U. S. Atomic Energy Commission, under Contract No. AT-(11-1)-GEN-8.

[1] F. H. Eisen, Phys. Rev. **123**, 736 (1961).

[2] For a recent review of the radiation damage work in III-V compound semiconductors see, for instance, J. W. Corbett, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Suppl. 7.

[3] J. W. Cleland and J. H. Crawford, Phys. Rev. **100**, 1614 (1955).

[4] U. Gonser and B. Okkerse, Phys. Rev. **105**, 757 (1957).

[5] R. Kaiser and H. Y. Fan, Phys. Rev. **138**, A156 (1965).

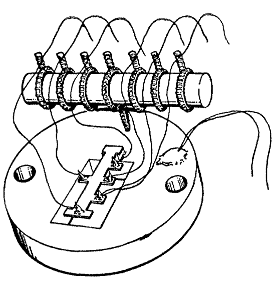

FIG. 1. Copper base plate with mounted sample and sapphire rod with tie points.

tained in this way. Copper-constantan thermocouples were used for the temperature measurements. One thermocouple was attached to one of the sample arms, another one was attached to the base plate. The base plate with the sample was inserted into a He cryostat, which has been described previously by Eisen.[6] The electrical resistivity and the Hall coefficient were measured with standard potentiometric techniques. The magnetic field used for the Hall measurements was 530 G.

Irradiations were performed with 1.0-MeV electrons from a Van de Graaff generator. The electron energy was determined by a double 60° magnet system calibrated at 1.66 MeV with the $\mathrm{Be}^9(\gamma,n)\mathrm{Be}^8$ reaction. A 0.006-mm aluminum scattering foil was placed in the path of the electron beam 6 cm above the sample to ensure uniform irradiation density across the sample. Judged by the radiation-induced mobility change in different regions of the sample, the flux was uniform over the sample area within 2%.

When liquid helium was used as a coolant during the irradiation, the sample temperature varied between 4.2°K and some higher temperature determined by the irradiation intensity. This undesirable sample heating was caused by the energy dissipation of the 1-MeV electrons in the sample and the bottom of the cryostat. When liquid nitrogen was used as a coolant during the irradiation, the sample temperature never exceeded 80°K.

Sample temperatures above the coolant temperature could be obtained with an electric heater which was built into the cryostat and maintained with a temperature controller within 0.1°K.

III. RESULTS AND DISCUSSION

A. Unirradiated Samples

The samples used in this work were p type and had carrier concentrations of about 1×10^{17} cm^{-3} near room temperature, which is typical for undoped GaSb. Following a common practice, the carrier concentrations quoted in this paper were calculated from the relation $R_H=1/ep$, where R_H is the Hall coefficient, e is the absolute value of the electronic charge, and p is the carrier concentration. In doing this, the distinction between light and heavy holes and the energy dependence of the carrier-scattering mechanisms is neglected. Therefore, p represents an "apparent carrier concentration" rather than the real carrier concentration, from which it may differ by as much as 50%. From the Hall coefficient R_H and the resistivity ρ, the Hall mobility $\mu_H=R_H/\rho$ can be obtained. For the samples used in this work the Hall mobility was ≈750 V^{-1} sec^{-1} cm^2 at 300°K, ≈3500 V^{-1} sec^{-1} cm^2 at 77°K, and had a maximum of ≈7000 V^{-1} sec^{-1} cm^2 near 30°K. These values appear to be typical for undoped GaSb.

The temperature dependence of the Hall coefficient for one of the samples is shown in Fig. 2. The circles represent the experimental data. The solid line corresponds to a one-acceptor level model with a level position $E_{A0}-E_v=0.040$ eV above the top of the valence band, an acceptor concentration $N_{A0}=1.38\times10^{17}$ cm^{-3}, a degeneracy factor $\lambda_{A0}=2$, and a density-of-state effective hole mass $m_h=0.4m_0$, where m_0 is the free-electron mass. The carrier concentration p for such a model is given by

$$p=\tfrac{1}{2}(-\eta+(\eta^2+4N_{A0}\eta)^{1/2});\qquad \eta=(N_v/\lambda_{A0})\exp[-(E_{A0}-E_v)/kT]. \tag{1}$$

($N_v=2[2\pi m_hkT/h^2]^{3/2}$ is the density of states of the valence band.)

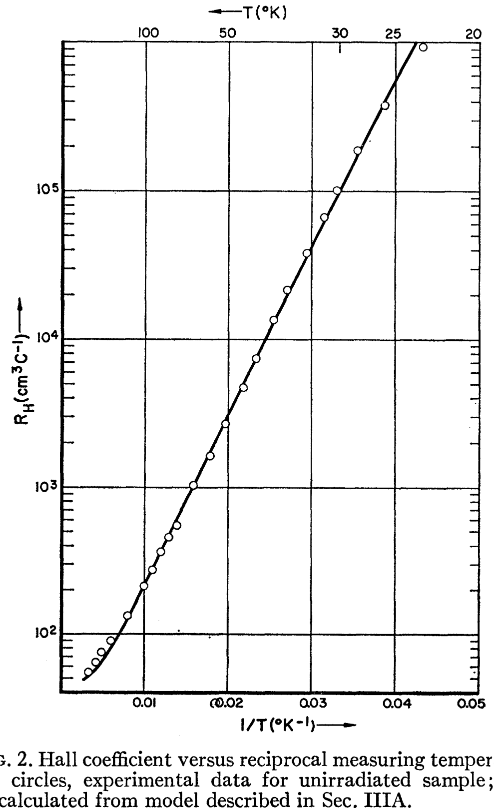

FIG. 2. Hall coefficient versus reciprocal measuring temperature. Open circles, experimental data for unirradiated sample; solid line, calculated from model described in Sec. IIIA.

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[6] F. H. Eisen, Advan. Cryog. Eng. 8, 437 (1963).

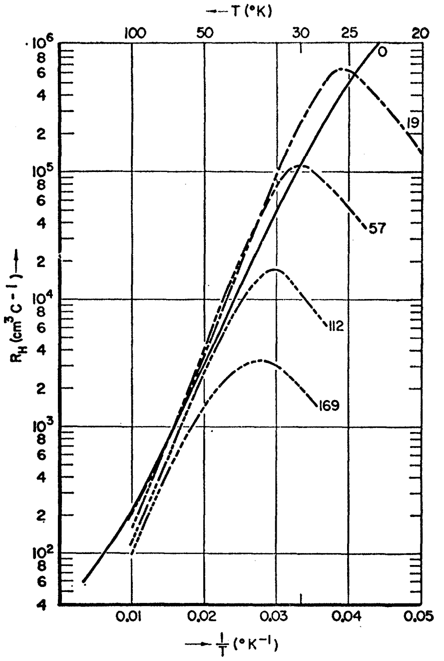

FIG. 3. Hall coefficient versus reciprocal measuring temperature after irradiation at 80°K with various doses. Numbers at the curves give dose in units of 10^{15} electrons cm^{-2}. Experimental points are omitted for the sake of clarity.

The nature of the defects, which are associated with the acceptor levels in undoped GaSb, is still not satisfactorily understood. It is believed that at least a substantial part of them is due to structural defects such as interstitials or vacancies or antistructure defects (Ga atom on Sb site) rather than to chemical impurities.[7]

Effer and Etter[8] reported values of 0.032 and 0.0365 eV for the acceptor level position governing the Hall-coefficient data in the range 30°–100°K in their samples *G*13 and *G*16, respectively. A comparison of their data with the data shown in Fig. 2 reveals that the slope of the Hall-coefficient curves for both their samples is somewhat smaller than the slope of the curve shown in Fig. 2. The reason for this discrepancy is not understood at the present time. Leifer and Dunlap[9] reported that they fitted their Hall-coefficient curve between 30 and 670°K with a model, assuming acceptor levels at 0.024 and 0.037 eV. Their curve runs somewhat lower but almost parallel to the curve shown in Fig. 2 of this paper, in the temperature range 30–300°K. It was found, however, that no fit of our data as good as the one shown in Fig. 2 could be obtained with the Leifer-Dunlap model.

It appears to the author that, while the question regarding the level structure of undoped GaSb is still not answered satisfactorily, the model used for the fit in Fig. 2 constitutes an adequate working basis for the present investigation.

B. Dose and Temperature Dependence of Radiation Effects

Although the recovery of the radiation-produced changes of the electrical resistivity and the Hall coefficient will be described in Sec. IIIC, it is necessary to state here that recovery was observed to start at $T\approx 110$°K. Therefore, measurements of the temperature dependence of the Hall coefficient and the resistivity of samples in which no recovery had occurred were restricted to temperatures below 110°K.

Figure 3 shows the dependence of the Hall coefficient on the measuring temperature after irradiation at $\approx$80°K with various doses. Irradiation had its largest effect on the Hall coefficient at low temperatures. In this region the curves corresponding to the irradiated sample exhibit a maximum, whose position shifts to lower Hall-coefficient values and higher temperatures as the irradiation dose increases. In the temperature region below the temperature of the maximum of the Hall coefficient, the slope of the resistivity curves (in a $\ln\rho$-versus-$1/T$ diagram) decreases rapidly with decreasing temperature (Fig. 4).

This behavior is characteristic for a material in which impurity conduction becomes increasingly competitive with the normal conduction mechanism towards lower

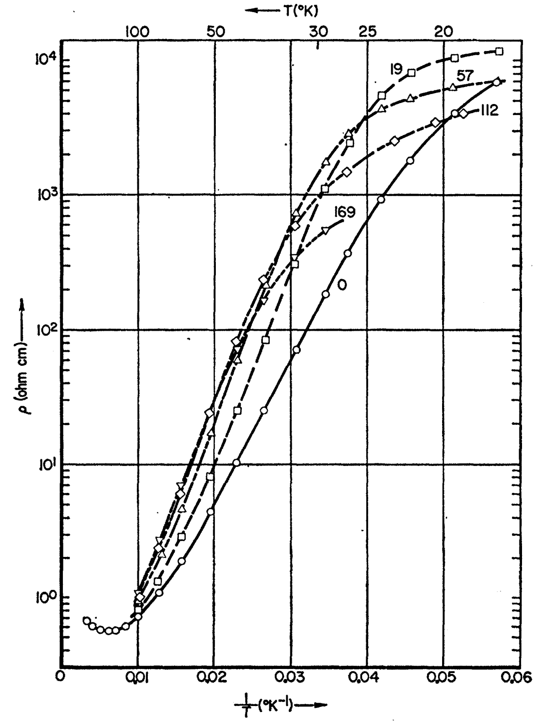

FIG. 4. Electrical resistivity versus reciprocal measuring temperature after irradiation at 80°K with various doses. Numbers at the curves give dose in units of 10^{16} electrons cm^{-2}.

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[7] R. D. Baxter, R. T. Bate, and F. I. Reid, J. Phys. Chem. Solids **26**, 41 (1965).

[8] D. Effer and P. I. Etter, J. Phys. Chem. Solids **25**, 451 (1964).

[9] H. N. Leifer and W. C. Dunlap, Phys. Rev. **95**, 51 (1954).

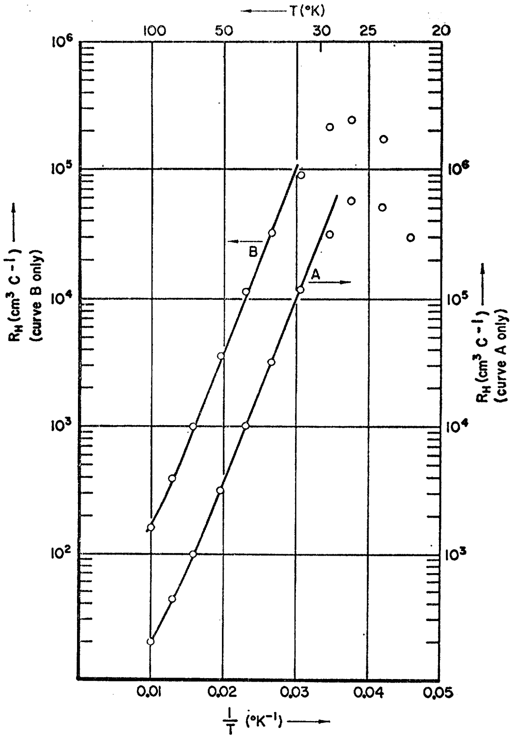

FIG. 5. Hall coefficient versus reciprocal measuring temperature. Open circles, experimental data; solid line, calculated from the model described in Sec. IIIB; curve A, after irradiation with 1.9×10^{16} electrons cm^{-2}; curve B, after irradiation with 5.7×10^{16} electrons cm^{-2}.

temperatures. The term "impurity conduction" normally refers to a charge-transport mechanism in which electrons or holes either move in an impurity band (high impurity concentration) or tunnel between neighboring impurity sites (low impurity concentration).[10] The temperature dependence of Hall coefficient and resistivity of irradiated samples observed in the present work suggest that impurity conduction occurs at low temperatures, but with radiation-produced defects acting as impurities.

At the temperature of the maximum of the Hall coefficient the impurity conductivity is approximately equal to the normal conductivity.[10] The shift of the position of the Hall-coefficient maximum with increasing dose is then interpreted as being due to three factors: (1) increase of the impurity conductivity due to increase of the defect concentration, (2) decrease of the hole concentration in the valence band due to an increasing amount of radiation-produced donors. (For reasons which are discussed below, the decrease of the hole concentration is apparent in the Hall-coefficient curves only after irradiation with doses smaller than 7.5×10^{16} electrons cm^{-2}.) (3) Decrease of the mobility of the holes in the valence band due to the increasing amount of scattering centers introduced by the irradiation. All three factors favor charge transport via impurity conduction relative to the ordinary conduction mechanism.

At higher temperatures, where impurity conduction does not contribute substantially to charge transport, surprisingly small changes of the Hall coefficient were produced by the irradiation. Near 100°K the Hall coefficient decreases slightly with increasing dose, but at the same time the slope of the curves increases. This causes an intersection of the Hall-coefficient curves which correspond to doses smaller than 7.5×10^{16} electrons cm^{-2} near 65°K. For higher doses no further increase of the slope occurs, and additional irradiation results in a downward shift in the Hall-coefficient curves, essentially parallel to themselves in the "high-temperature" region.

The temperature dependence of the Hall coefficient after irradiation with doses smaller than 7.5×10^{16} electrons cm^{-2} indicates that both acceptors and donors were produced by the irradiation and that the acceptor production rate was somewhat larger than the donor production rate. An attempt to account for the observed temperature dependence of the Hall-coefficient curves quantitatively is faced with the difficulty that in an ill-defined temperature range at the high-temperature side of the Hall-coefficient maximum, impurity conduction still makes a significant contribution to the charge transport. Therefore, in this range the experimentally observed values of the Hall voltage are smaller than they would be if no impurity conduction would occur. Quantitative analysis of the Hall-coefficient data is restricted to temperatures at which impurity conduction can be neglected. Since the maximum of the Hall coefficient occurs at fairly high temperatures after high irradiation doses, one is restricted to the low-dose curves in order to have a reasonably large temperature range for the curve fitting.

An attempt has been made to fit the Hall-coefficient curve after irradiation with 1.9×10^{16} electrons cm^{-2} on the basis of a model in which one type of radiation-produced acceptors ($A1$) and radiation-produced donors (D) are assumed in addition to the residual acceptors ($A0$). The term "residual acceptors" is used for those acceptors which are present in the sample prior to the irradiation. Assuming that the donors are completely ionized, the temperature dependence of the carrier concentration was evaluated from graphical solutions of the equation

$$p+p_{A0}+p_{A1}+N_D=N_{A0}+N_{A1}, \qquad (2)$$

where p is the concentration of holes in the valence band, p_{Ai} is the concentration of holes bound to the acceptors Ai ($i=0$ or 1), N_{A0} is the concentration of the residual acceptors, and N_D and N_{A1} are the concentrations of radiation-produced donors and acceptors, respectively.[11]

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[10] N. F. Mott and W. D. Twose, Advan. Phys. **10**, 107 (1961).

[11] W. Shockley, *Electrons and Holes in Semiconductors* (D. van Nostrand Company, Inc., Princeton, New Jersey, 1959), p. 465.

Curve A in Fig. 5 was obtained with the following parameter values: $m_h=0.4m_0$; $E_{A0}-E_v=0.040$ eV; $N_{A0}=1.38\times10^{17}$ cm^{-3}; $\lambda_{A0}=2$; $E_{A1}-E_v=0.023$ eV; $N_{A1}=3.27\times10^{16}$ cm^{-3}; $\lambda_{A1}=2$; $N_D=1.50\times10^{16}$ cm^{-3}. Note that the values for m_h, E_{A0}, N_{A0}, and λ_{A0} were taken from the fit of the Hall-coefficient curve for the unirradiated sample. Therefore, the only adjustable parameters were E_{A1}, N_{A1}, N_D, and λ_{A1}.

If in this model the values for N_{A1} and N_D are increased by a constant multiplicative factor, simulating a higher irradiation dose, then Hall-coefficient curves with steeper slopes and lower Hall-coefficient values at 100°K are obtained. This behavior was observed experimentally for curves corresponding to doses $\leqq 7.5\times10^{16}$ electrons cm^{-2}.

Curve B in Fig. 5 was constructed from the model with values for N_{A1} and N_D three times as large as those for curve A. The agreement with the experimental data, obtained after irradiation with 5.7×10^{16} electrons cm^{-2}, is very satisfactory. For doses higher than 5.7×10^{16} electrons cm^{-2}, the model predicts Hall-coefficient curves which approach an asymptotic curve, deviating from curve B in Fig. 5 only by a few percent at temperatures below 50°K. Experimentally, a different behavior was observed, but this is most probably due to the fact that after higher irradiation doses, i.e., higher defect concentrations, impurity conduction caused a noticeable modification of the Hall-coefficient curves even at temperatures above 50°K.

The numerical values of N_{A1}, N_D, E_{A1}, and λ_{A1} derived from the analysis of the Hall-coefficient curves should be viewed with some caution. The curve fitting is quite sensitive to the values of E_{A1} and $(1+\lambda_{A1})N_D/N_{A1}$ but less sensitive to the absolute values of N_{A1}, N_D, and λ_{A1}. Moreover, the simplifications made in the calculation of the carrier concentrations from the Hall-coefficient values (see Sec. IIIA) may affect the values of the parameters. Taking all this into account, it is believed that the values for E_{A1} and $(1+\lambda_{A1})N_D/N_{A1}$ are correct within about 15% and the absolute values for N_{A1} and N_D within a factor of 2.

It is emphasized that in the present work the Fermi level was confined to the range 0.025 to 0.035 eV above the valence band. Therefore, acceptor levels with positions higher than $\approx$0.05 eV above the valence band could not be detected by the Hall measurements.

The model outlined above clearly is the most simple one which can account satisfactorily for the experimental data. Although it imposes no limitation on the number of different types of radiation-produced donors [N_D in Eq. (2) is simply the sum of all radiation-produced donors], it assumes only one type of radiation-produced acceptors. The possibility of fitting the data with a model which assumes more than one radiation-produced acceptor level has not been explored yet. Such an effort does not seem to be warranted at the present time. However, one should be alert to the possibility that more than one type of acceptors may have been produced by the irradiation.

A monotonic decrease of the Hall mobility with increasing dose was observed at all temperatures. The circles in Fig. 6 show the experimentally observed change of the reciprocal Hall mobility after an irradiation with 1.9×10^{16} electrons cm^{-2} as a function of the measuring temperature. At low temperatures $\Delta(1/\mu_H)$ varies approximately with T^{-2}. However, as the temperature increases, the curve bends over and above 70°K there appears to be even a slightly positive slope.

The following effects may contribute to the observed change of the Hall mobility:

(1) The radiation-produced defects act as additional scattering centers. Some of these defects may act as neutral, others as ionized scattering centers.

(2) Because of the radiation-induced change of the Fermi level position, the charge state and therefore the scattering power of some of the residual defects is changed.

(3) Because of the radiation-induced change of the carrier concentration, a change in the screening of the ionized residual defects occurs, which changes the scattering power of these defects.

(4) Because of the radiation-induced change of the carrier concentration, the interaction of charge carriers with optical phonons is changed.

The effects listed under (3) and (4) are believed to be small for small changes of the carrier concentration. In the present case, the changes of the carrier concentration are smaller than 7×10^{14} cm^{-3}, and neglecting these effects is therefore justified. Considering only contributions from the effects listed under (1) and (2), an approximate evaluation of the radiation-induced change of the drift mobility μ can be made using the method of the addition of the reciprocal mobilities:

$$\left(\Delta\frac{1}{\mu}\right)_{\text{tot}}\approx\frac{1}{\mu_i}+\frac{1}{\mu_N}+\left(\Delta\frac{1}{\mu}\right)_R. \tag{3}$$

The first and second terms on the right-hand side of Eq. (3) are the contributions from ionized and neutral radiation-produced defects, respectively, while the third term is the contribution of those residual defects whose charge state is changed by the irradiation.

For temperatures below the Debye temperature ($\Theta_D\approx280$°K for GaSb), Eq. (3) is a satisfactory approximation only if the scattering of carriers by optical phonons is negligible. Wagini[12] has concluded from his measurements of galvanomagnetic and thermoelectric properties that in undoped GaSb, scattering by acoustical phonons is the dominant scattering mechanism at room temperature. If this is true, neglect of optical-phonon scattering at temperatures below 100°K is justified.

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[12] H. Wagini, Z. Naturforsch. **20a**, 1317 (1965).

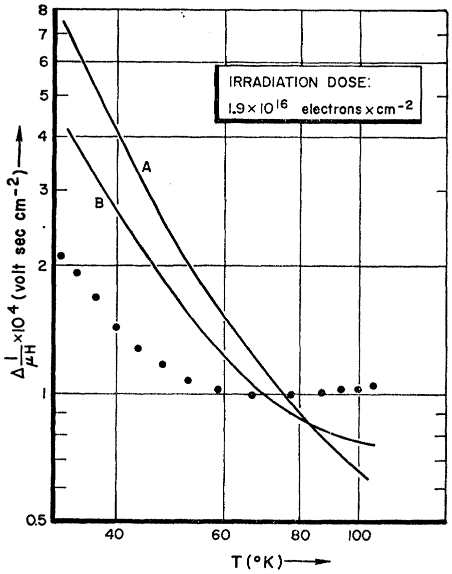

FIG. 6. Radiation-induced change of the reciprocal Hall mobility versus measuring temperature after irradiation with 1.9×10^{16} electrons cm^{-2}. Full circles, experimental data; curves A and B, calculated from models described in Sec. IIIB.

Assuming that only single-ionized and neutral defects were produced and using the expressions derived by Brooks and Herring[13] for ionized impurity scattering and by Erginsoy[14] for neutral impurity scattering, Eq. (3) may be rewritten as

$$\left(\Delta\frac{1}{\mu}\right)_{\text{tot}}\approx C_{\text{ion}}\Delta N_{\text{ion}}+C_{\text{neut}}\Delta N_{\text{neut}}\,, \tag{4}$$

where

$$C_{\text{ion}}=\frac{\pi^{3/2}m_h{}^{1/2}e^3}{2^{7/2}\epsilon^2k^{3/2}T^{3/2}}\left[\ln(1+b)-\frac{b}{1+b}\right], \tag{5}$$

with

$$b=6\epsilon m_hk^2T^2/\pi ph^2e^2$$

and

$$C_{\text{neut}}=5\epsilon h^3/2\pi^3m_he^3. \tag{6}$$

In Eqs. (4)–(6), ϵ is the static dielectric constant, ΔN_{ion} and ΔN_{neut} are the radiation-induced changes of the concentration of ionized and neutral defects, respectively, and the other symbols have their usual meaning.

Using the model developed above, one obtains

$$\Delta N_{\text{ion}}=N_{A1}{}^*+N_D+\Delta N_{A0}{}^*, \tag{7}$$

$$\Delta N_{\text{neut}}=N_{A1}-N_{A1}{}^*-\Delta N_{A0}{}^*, \tag{8}$$

where the asterisk symbolizes the ionized state and $\Delta N_{A0}{}^*$ is the radiation-induced change in the concentration of the ionized residual acceptors.

For not too high irradiation doses, values for N_D, N_{A1}, $N_{A1}{}^*$, and $\Delta N_{A0}{}^*$ can be obtained from the experimentally observed temperature dependence of the Hall coefficient using the curve-fitting procedure described above.

Note that, as a consequence of the assumption $R_H=1/ep$, the Hall mobility μ_H becomes equal to the drift mobility μ. Using Eqs. (4)–(8), one should then be able to calculate the radiation-induced change of the reciprocal Hall mobility from the temperature dependence of the Hall coefficient measured after the irradiation.

Curve A in Fig. 6 shows the result of such a calculation for a sample irradiated with 1.9×10^{16} electrons cm^{-2} at 80°K. The agreement with the experimental data is poor. The calculated values of $\Delta(1/\mu_H)$ are too large by a factor of 3 at low temperatures and there is little tendency of the theoretical curve to level off towards higher temperatures. This behavior is mainly due to the fact that ΔN_{ion} is considerably larger than ΔN_{neut} in the entire temperature range shown in Fig. 6 and that C_{ion} is strongly temperature-dependent.

In writing Eqs. (7) and (8) it has been assumed that the distance between any two defects is sufficiently large to treat them as independent scattering centers. On the other hand, it is to be expected that a substantial fraction of the defects produced by 1-MeV electrons in GaSb are close pair Frenkel defects with a distance between vacancy and interstitial of only some 10 Å. Consider then the case that, within the framework of the model developed above, each radiation-produced donor is located close to a radiation-produced acceptor. There will be $N_{A1}{}^*N_D/N_{A1}$ close pairs with a positively charged donor and a negatively charged acceptor. Clearly, it is not permissible to treat the two components of such a pair as independent ionized scattering centers. In a first approximation such a close pair rather may be treated as one neutral scattering center. There are other close pairs in which the acceptor is neutral but the donor is ionized. Taking the close distance between the two components of such a pair into account even in a first approximation would be rather difficult. Fortunately,

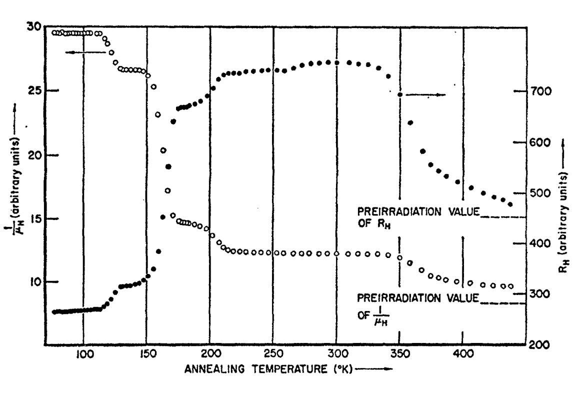

FIG. 7. Isochronal pulse annealing between 77 and 437°K after irradiation with 1×10^{17} electrons cm^{-2} at $T\leqq25$°K. Full circles, Hall coefficient at 77°K; open circles, reciprocal Hall mobility at 77°K.

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[13] Quoted by E. Conwell and P. P. Debye, Phys. Rev. 93, 693 (1954).

[14] C. Erginsoy, Phys. Rev. 79, 1013 (1950).

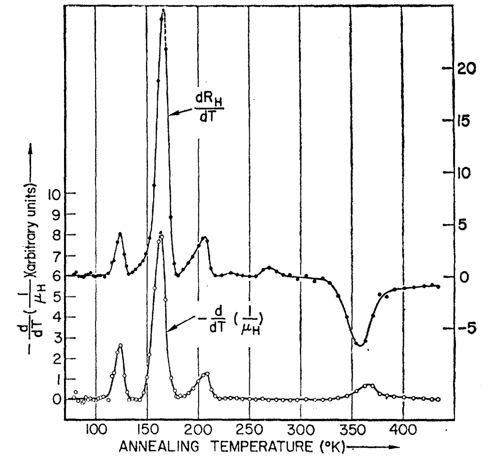

FIG. 8. Temperature derivatives of the isochrones shown in Fig. 7.

the number of these close pairs is only a small fraction of the total number of radiation-produced defects, so that only a small error in the evaluation of $(\Delta 1/\mu)_{\text{tot}}$ is introduced by treating their neutral and ionized components as independent scattering centers. Instead of Eqs. (7) and (8) one obtains then

$$\Delta N_{\text{ion}} = N_{A1}^* - (N_D N_{A1}^*/N_{A1}) + N_D(1 - N_{A1}^*/N_{A1}) + \Delta N_{A0}^*, \quad (9)$$

$$\Delta N_{\text{neut}} = N_{A1} - N_{A1}^* + (N_D N_{A1}^*/N_{A1}) - \Delta N_{A0}^*. \quad (10)$$

Curve B in Fig. 6 shows the temperature dependence of $\Delta(1/\mu_H)$ calculated from Eqs. (4)–(6), (9), and (10). The agreement with the experimental data is still only fair. However, considering the various approximations entering into the calculation of $\Delta(1/\mu_H)$, a much better agreement can hardly be expected. Therefore, it is believed that the model corresponding to curve B in Fig. 6 should be regarded as a possible interpretation.

C. Annealing Experiments

Because of the increase of the sample temperature during the irradiation, the recovery of the radiation-produced damage could be studied only for temperatures above 15°K. No recovery was observed between 15° through 77°K, which would evidence itself in a change of the electrical conductivity measured at 14°K. The Hall coefficient proved not to be a very useful property for recovery studies below liquid-nitrogen temperature because at low temperatures it could not be measured with the precision needed for the detection of small amounts of recovery. Within the accuracy of the measurements (approximately 10%) no change in the Hall coefficient due to recovery between 25 and 77°K was observed in a sample irradiated with 2×10^{16} electrons cm^{-2} at $T\leqq 25$°K.

Both the Hall mobility and the Hall coefficient, measured at 77°K, were used as defect-sensitive quantities for recovery studies above 77°K. The results of an isochronal pulse annealing after irradiation with 1×10^{17} electrons cm^{-2} at $T\leqq 25$°K are shown in Fig. 7. The length of each heating pulse was 10 min. Major recovery stages are seen to occur for both properties near 122°, 163°, 203°, and 365°K, which shall be referred to as stages I through IV, in order of increasing temperature. A plot of the temperature derivatives of the curves of Fig. 7 reveals an asymmetry of the stage-III peak (Fig. 8). Most likely, this asymmetry indicates two unresolved peaks, corresponding to two recovery processes with nearly the same activation energy.

After annealing up to 437°K, neither the Hall mobility nor the Hall coefficient had returned to their preirradiation values. Annealing at higher temperatures could not be performed easily because of the melting of the solder which was used for the sample mounting. However, one sample supported by a small glass plate was annealed at 573°K for 1 h. This treatment resulted in a further slight decrease of the reciprocal Hall mobility, without reaching the preirradiation value. The Hall coefficient decreased slightly below its preirradiation value.

Isothermal recovery studies of both the Hall coefficient and the Hall mobility were performed at 119, 159, 202, and 365°K. The time dependence of the unrecovered fraction of the reciprocal Hall mobility change in a particular stage is shown for each of the four stages in Fig. 9. For stages I–III, the beginning and end of each stage is rather well defined. Unfortunately, the same is not true for the end of stage IV. In the isochronal data a continuous decrease of the reciprocal Hall mobility and the Hall coefficient is observed up to 437°K, which was the highest temperature in this experiment. The negative slopes of the recovery curves in Fig. 7, however, decrease rather rapidly near 380°K. It seems likely that the recovery observed above ≈400°K is not due to the same process which causes the more pronounced recovery near 365°K. The data for $T=365$°K in Fig. 9 were obtained under the assumption that the recovery

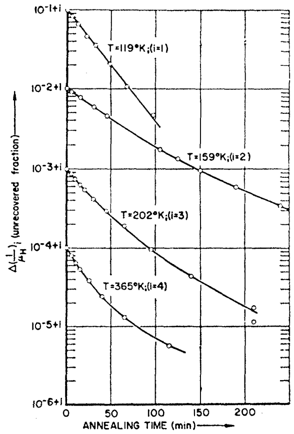

FIG. 9. Isothermal annealing of the reciprocal Hall mobility at the indicated temperatures after irradiation with 1×10^{17} electrons cm^{-2} at $T\leqq 25$°K. Measurements were made at 77°K.

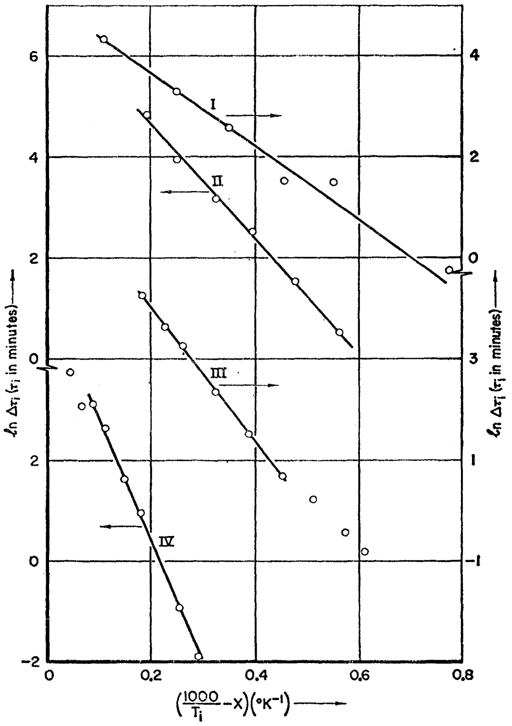

FIG. 10. $\ln\Delta\tau_i$ versus $1/T_i$ for each of the recovery stages I–IV. The meaning of $\Delta\tau_i$ and T_i is explained in Sec. IIIC. The scale for $\ln\Delta\tau_i$ is indicated by the arrow for each of the stages. X takes the following values: stage I, 7.5; stage II, 5.5; stage III, 4.3; stage IV, 2.5.

due to the process of interest was complete at 395°K and that no background recovery due to other processes occurred below this temperature. This is admittedly an oversimplification of the true state of affairs.

From a combination of the isochronal and isothermal annealing results, the activation energies for the recovery stages I–IV were evaluated using the Meechan-Brinkman method.[15] This method requires two identical samples, i.e., two samples with the same history which have been irradiated with the same dose under the same conditions. With one sample an isochronal annealing study and with the other an isothermal annealing study is performed. For the evaluation of the activation energy the quantity $\ln\Delta\tau_i$ is plotted versus $1/T_i$, where $\Delta\tau_i$ is the isothermal time equivalent of the isochronal heating pulse at temperature T_i. For recovery processes which are governed by a unique activation energy, this plot yields a straight line and the activation energy is obtained from its slope. In practice it is difficult to fulfill the condition of identical samples. In the present case the same sample was used for both the isochronal and isothermal annealing. After a first irradiation the sample was annealed isochronally from 77 to 437°K. Subsequently, it was reirradiated with the same dose as the first time and then isothermal anneals were performed at 119, 159, 202, and 365°K. It was assumed that the small amount of damage remaining in the sample at the end of the isochronal anneal would constitute only a negligible deviation from the condition of identical samples.

Using the reciprocal Hall mobility in one case and the Hall coefficient in the other case as the defect-sensitive property, two independently determined values were obtained for the activation energy of each of the stages I–IV. Both sets of activation energy values are listed in Table I, and are seen to be in good agreement with each other. As an example, Meechan-Brinkman plots, based on the Hall mobility recovery, are shown in Fig. 10. Systematic deviations from the straight-line behavior are noted at the low-temperature end of the curve corresponding to stage III and at the high-temperature end of the curve corresponding to stage IV. In the case of stage III, this is another indication that the recovery in this stage is due to two unresolved recovery processes. Evidence for this had been obtained already from the derivative plots in Fig. 8. The activation energy derived from the Meechan-Brinkman plot corresponds to the high-temperature component of the unresolved doublet. The deviation from straight-line behavior at the high-temperature end of the Meechan-Brinkman plot for stage IV is most probably due to the aforementioned difficulties in the cutoff procedure.

If we assume that the change of the reciprocal Hall mobility which occurs in a particular stage is proportional to the concentration of defects, which are removed in this stage, then it can be concluded from the isotherm at 119°K in Fig. 9 that in stage I the recovery obeys first-order kinetics. This and the fact that stage-I recovery requires the least amount of thermal activation favors the interpretation that in this stage annihilation of close pairs occurs. However, if the time constant τ of the isothermal recovery at 119°K is expressed in the form

$$\tau^{-1}=\nu_{\mathrm{eff}}\times\exp(-E_m/kT), \qquad (11)$$

one obtains $\nu_{\mathrm{eff}}=8\times10^9$ sec^{-1}, with $E_m=0.31$ eV. This value for the effective-frequency factor is at least two orders of magnitude lower than what one would expect for close pair recombination. The reason for this low value is not understood at the present time.

If the isothermal recovery in stages II–IV is analyzed in terms of the phenomenological equation

$$\frac{d}{dt}\left(\Delta\frac{1}{\mu_H}\right)_i=-K_i\times\left(\Delta\frac{1}{\mu_H}\right)_i^{\gamma_i}, \qquad (12)$$

where $(\Delta 1/\mu_H)_i\equiv 1/\mu_H-1/\mu_{H,i}$, $1/\mu_{H,i}$ is the reciprocal Hall mobility at the end of the ith stage, and the K_i's are constants, then the following values for γ_i are obtained: $\gamma_2=1.25$, $\gamma_3=1.20$, and $\gamma_4=1.70$. The nonintegral values of the γ_i indicate a complex nature of the recovery in the stages II–IV.

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[15] C. J. Meechan and J. A. Brinkman, Phys. Rev. **103**, 1193 (1956).

TABLE I. Center temperatures T_c and activation energies E for major annealing stages.

Stage	T_c(°K)	E(eV) (Hall mobility)	E(eV) (Hall coeff.)
I	122	0.31	0.30
II	163	0.47	0.50
III	203	0.58	0.56
IV	365	1.07	1.01

Figure 11 shows the temperature dependence of the Hall coefficient of a sample which had been irradiated with 1×10^{17} electrons cm^{-2} at $T\leqq25$°K and subsequently annealed isochronally. The temperature associated with each curve indicates the temperature up to which the sample has been annealed prior to the measurement of the Hall-coefficient curve. In the temperature region in which the Hall coefficient is not or only slightly influenced by the impurity conduction, annealing through the stages I–III results essentially in a successive shift of the Hall-coefficient curve towards higher Hall-coefficient values with hardly any change of the slope. This indicates a concurrent removal of acceptors and donors in each of the stages I–III.

The Hall-coefficient curve obtained after annealing at 218°K intersects the curve for the unirradiated sample at $\approx$150°K. The same crossover temperature was found for a sample which had been irradiated with 1.9×10^{16} electrons cm^{-2} and subsequently annealed at 300°K. Since no significant changes of the Hall-coefficient curve are produced by annealing at temperatures between 218 and 300°K, it can be concluded that the crossover temperature is independent of the irradiation dose. It may be compared then with the crossover temperature of 65°K found for samples after irradiation at 80°K with not too high doses (Fig. 3). (For higher doses no intersection with the curve for the unirradiated sample was observed because of the influence of the impurity-conduction mechanism.)

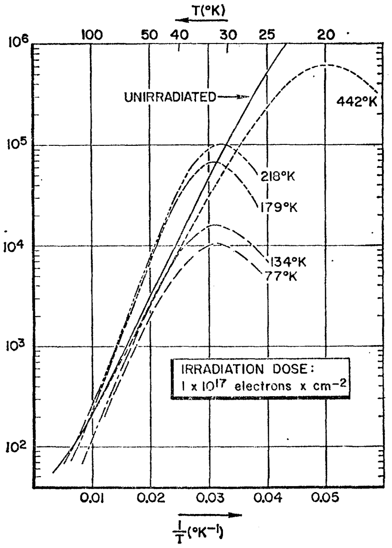

FIG. 11. Hall coefficient versus reciprocal measuring temperature before irradiation and after irradiation with 1×10^{17} electrons cm^{-2} at $T\leqq25$°K followed by annealing to successively higher temperatures. The temperature at the curves indicate the highest temperature up to which the sample had been annealed, before the Hall-coefficient curve was measured. Experimental points are omitted for the sake of clarity.

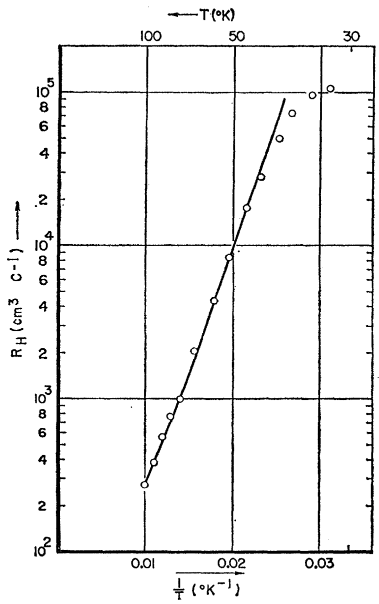

FIG. 12. Hall coefficient versus reciprocal temperature. Open circles, experimental data after irradiation with 1×10^{17} electrons cm^{-2} at $T\leqq25$°K and subsequent annealing up to 218°K; solid line, calculated from model described in Sec. IIIC.

If the recovery which occurred between 110 and 218°K would have involved only annihilation of the radiation-produced acceptors and donors, then the shift in the crossover temperature would indicate removal of a larger fraction of acceptors than donors. But then the annealing should have resulted also in a steeper slope of the Hall-coefficient curve. Since no substantial change of the slope was observed, it appears that in addition to the annihilation of radiation-produced acceptors and donors, other processes occurred during the recovery between 110 and 218°K.

It is conjectured that interaction between some of the radiation-produced defects and the residual acceptors may have occurred. In the most simple case this could result in the removal of some of the $A0$ levels. Figure 12 shows that a satisfactory fit of the Hall-coefficient data obtained after irradiation at $T\leqq25$°K with 1×10^{17} electrons cm^{-2} and subsequent annealing up to 218°K can be achieved with the following values for the defect concentrations: $N_{A0}=1.08\times10^{17}$ cm^{-3}, $N_{A1}=4.5\times10^{16}$ cm^{-3}, $N_D=3.5\times10^{16}$ cm^{-3}.

Unfortunately, no quantitative analysis of the Hall-coefficient curve measured before the annealing can be made because of the strong effect of impurity conduction. However, using the data of the analysis of the Hall-coefficient curves after low-dose irradiation and assuming a linear-defect production rate, the concentration of radiation-produced acceptors and donors before the annealing can be estimated as 2×10^{17} and 9×10^{16} cm^{-3}, respectively. Thus annealing from 110 to 218°K would have produced approximately the following changes of defect concentrations: $-\Delta N_{A0}\approx3\times10^{16}$ cm^{-3}, $-\Delta N_{A1}\approx1.6\times10^{17}$ cm^{-3}, $-\Delta N_D\approx6\times10^{16}$ cm^{-3}.

After annealing up to 442°K the Hall coefficient has almost completely returned to its preirradiation value if measured at temperatures above 80°K (Fig. 11). The deviation from the preirradiation curve, noticeable below 80°K, could be caused by as little as 10^{14} shallow acceptors per cm^3. Clearly, if any of the radiation-produced defects became trapped at residual defects during the annealing between 110 and 218°K, they must have been released by the annealing between 340 and 440°K.

IV. SUMMARY AND CONCLUSIONS

The effect of low-temperature irradiation with 1.0-MeV electrons on the Hall coefficient and the Hall mobility of undoped GaSb has been investigated and a study of the recovery of the radiation-produced changes of these properties has been made. From the radiation-induced changes of the Hall coefficient it was concluded that both acceptors and donors are created by the irradiation and that the production rate of the acceptors is larger than the production rate of the donors. It has been shown that the temperature dependence of the Hall coefficient after not too high irradiation doses is in quantitative agreement with a model which is characterized by radiation-produced acceptors with levels 0.023 eV above the valence band and completely ionized donors. Deviations from the predictions of the model, which occur at doses higher than 7.5×10^{16} electrons cm^{-2}, are ascribed to the increasing influence of impurity conduction. The temperature dependence of the change of the reciprocal Hall mobility has been found to be also in fair agreement with this model if it is assumed that some of the radiation-induced acceptors and the donors are introduced as close pairs. It has been pointed out that this model, although it accounts satisfactorily for the observed effects, should be considered as a tentative explanation. At the present time it is distinguished from other possible models by what appears to be a minimum of arbitrary assumptions.

No recovery was observed between 15 and 110°K. Major recovery stages were found near 122, 163, 203, and 365°K. The activation energies corresponding to these stages were measured as 0.31±0.02, 0.48±0.03, 0.57±0.03, and 1.0±0.1 eV. The recovery stage near 122°K was found to obey first-order kinetics and is tentatively ascribed to close pair recombination. No simple kinetics were found for the other stages.

The temperature dependence of the Hall coefficient measured after low-temperature irradiation and subsequent annealing indicated concurrent removal of acceptors and donors in each of the recovery stages I–IV. It was conjectured that interaction between radiation-produced defects and residual acceptors occurred during warmup to 218°K.

After annealing up to 440°K, most of the radiation-produced defects have disappeared; however, even after annealing at 573°K the material had not returned completely to its preirradiation state.

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