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Annealing of ^{60}Co-Gamma-Irradiated Germanium*

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Annealing of changes in reciprocal mobility and carrier concentration induced by ^{60}Co gamma irradiation at 77°K in germanium doped with either arsenic or antimony has been investigated by an isochronal annealing technique for materials whose initial carrier concentration ranged from 5×10^{13} to 5×10^{15} cm^{-3}. Four annealing stages were observed. The annealing of one stage in the room-temperature range was found to be dependent on the concentration and type of impurity. The data are discussed in terms of a speculative model based upon an analogy with defect behavior observed in silicon.

I. INTRODUCTION

THE impurity-dependent annealing behavior of the radiation-induced changes in the carrier concentration and mobility of germanium was first reported by Brown *et al.*[1] They found that Sb-doped material showed considerably more recovery in the carrier concentration than As- or P-doped material when the samples irradiated at 80°K were annealed at 56°C. They also found that the variation in reciprocal mobility could be correlated with the change in carrier concentration for the anneal of Sb-doped samples but not for As-doped samples. These results were interpreted as indicating that defect-impurity complexes formed more readily for some impurities than for others. In a subsequent investigation by Curtis and Crawford,[2] additional evidence for the existence of a defect-impurity interaction was found. It was shown that recovery of changes of minority carrier lifetime induced by ^{60}Co gamma irradiation at 35°C was influenced not only by the impurity type but also by impurity concentration in both As- and Sb-doped samples. The annealing rate increased in each case with an increase in impurity concentration, but more extensive recovery of lifetime was produced in Sb-doped samples by a given anneal in the range from 340 to 380°K.

The influence of impurity type on the annealing properties of carrier concentration in ^{60}Co-gamma-irradiated Ge has also been reported by Ishino *et al.*[3] They found a complex annealing process which indicated a range of activation energies from 0.8 to 1.4 eV for As-doped material, depending on the section of the curves being analyzed, and 1.2 eV for Sb-doped material. Their results were interpreted in terms of independent annealing of the interstitial and vacancy. Isothermal-annealing studies of ^{60}Co-gamma-irradiated Sb-doped germanium by Pigg and Crawford[4] showed that the annealing in Sb-doped material was complex, but that the recovery could be interpreted without invoking the presence of a Ge interstitial. Vacancy-impurity complex formation was postulated as an intermediate stage in the annealing mechanism. They found that some sort of stable complex was formed by annealing in the temperature range from 377 to 455°K. The isothermal anneal reaching a plateau which was dependent upon the annealing temperature. A 377°K anneal saturated with about 50% of the radiation induced change in carrier concentration remaining. A sample annealing at 455°K reached a plateau with only 25% of the radiation induced change in carrier concentration remaining. However, much more than a simple temperature-dependent saturation is involved since samples annealed to a plateau at 377°K showed no further change in carrier concentration when they were subsequently annealed at 455°K.

The full dimensions of the possibilities of defect-impurity interactions and complex formation are shown by the spin-resonance studies of Si that have been irradiated and annealed by Bemski,[5] and Watkins and co-workers.[6–9] Among the identified centers are isolated vacancies, vacancy-oxygen complexes, vacancy-substitutional impurity complexes, divacancies, and interstitial impurities. There are indications suggesting the presence of impurity-multivacancy complexes and the migration of interstitial impurity atoms. In view of the similarity between Si and Ge, it would not be surprising to find analogous complexes in germanium. The work reported here was performed to explore further the effect of defect-impurity interaction in the annealing of the irradiation-induced change in carrier concentration and mobility.

In this paper, we discuss the isochronal annealing of carrier concentration and reciprocal mobility in *n*-type germanium for a range of initial carrier concentrations

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[1] W. L. Brown, W. M. Augustyniak, and T. R. Waite, J. Appl. Phys. **30**, 1258 (1956).
[2] O. L. Curtis, Jr., and J. H. Crawford, Jr., Phys. Rev. **126**, 1342 (1962).
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[4] J. C. Pigg and J. H. Crawford, Jr., Phys. Rev. **135**, A1141 (1964).
[5] G. Bemski, J. Appl. Phys. **30**, 1195 (1959).
[6] G. D. Watkins, J. W. Corbett, and R. M. Walker, J. Appl. Phys. **30**, 1198 (1959).
[7] J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. MacDonald, Phys. Rev. **121**, 1015 (1961).
[8] G. D. Watkins and J. W. Corbett, Phys. Rev. **134**, A1359 (1964).
[9] G. D. Watkins, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1965), Vol. 3, pp. 97–113.

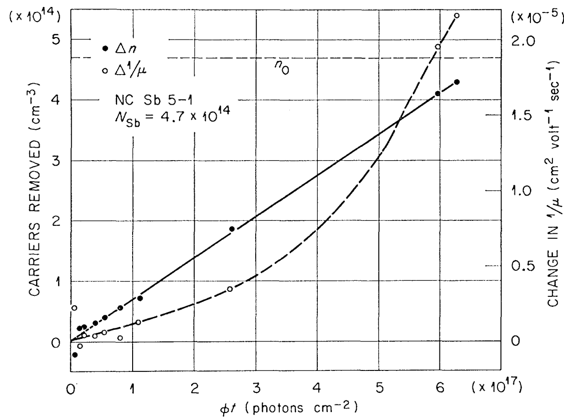

Fig. 1. Change in carrier concentration and reciprocal mobility due to ^{60}Co gamma irradiation. Antimony concentration 4.7×10^{14}.

from 5×10^{13} to 5×10^{15} cm^{-3} due to both arsenic and antimony doping after ^{60}Co-gamma irradiation at liquid-nitrogen temperature.

II. EXPERIMENTAL PROCEDURE

The samples used were *n*-type germanium single crystals doped with arsenic or antimony to impurity concentrations varying between 5×10^{13} to 5×10^{15} atoms/cm^3. To insure a minimum impurity gradient, discs were cut from the ingots perpendicular to the direction of growth. Bridgeshaped samples were cut from the central sections of the discs using an ultrasonic cutting die. The samples were etched with CP4 etch. After applying soldered ohmic contacts, the samples were mounted in the slot of a sample holder made from a bakelite stick, then covered by a phosphor bronze strip to prevent breakage in handling. The bronze strip was covered by cellulose acetate tape to provide electrical insulation and physical separation from the sample. Adequate isolation was thus achieved without introducing undue thermal lag.

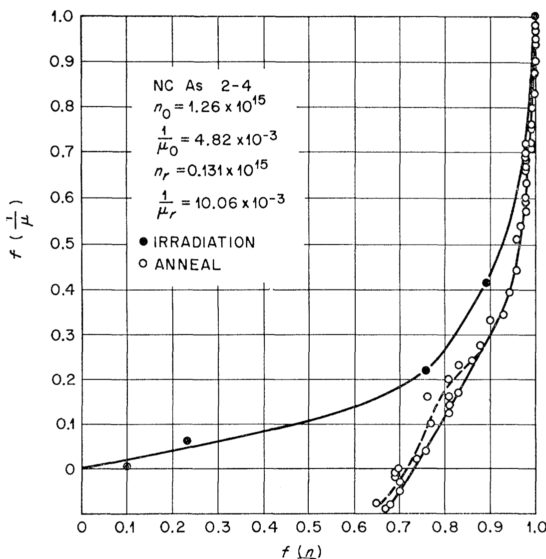

Fig. 2. The relation between the changes in carrier concentration and reciprocal mobility. Arsenic concentration 1.26×10^{15}.

The Hall coefficient and resistivity were measured over a temperature range from 77 to 300°K prior to irradiation. The irradiations were performed in a ^{60}Co gamma field whose intensity at the sample, as measured by cerrous sulphate dosimetry, was 5.6×10^6 R/h or 8.8×10^{15} photons/cm^2 h. The specimens were immersed in liquid nitrogen during the irradiation. They were removed periodically from the irradiation facility for measurement of Hall coefficient and resistivity. The physical void around the sample provided by the mounting technique remained filled with liquid nitrogen during removal from the irradiation facility to the transfer or storage Dewar. Consequently, the samples were continuously in liquid nitrogen from the beginning of the irradiation until the first anneal. The irradiation was continued until about 90% of the initial carrier concentration was removed.

The samples were isochronally annealed for 20-min periods with 5- and 10-°K steps between successive anneals. The Hall coefficient and resistivity were measured at liquid nitrogen temperature after each anneal. A second reference temperature of 273°K was added after the sample had been annealed at 275°K.

For every case the Fermi level is below 0.2 eV when these samples are at 273°K. Only those acceptor states below the Fermi level can contribute to the change in carrier concentration. The states which act as acceptors when the sample is at 273°K will be termed deep states. The states which are empty and do not act as acceptors when the sample is at 273°K will be termed shallow states. The shallow-state concentration is determined as the difference in carrier concentrations measured at 273°K and 77°K. This difference is primarily due to the level or levels near 0.2-eV below the conduction band, as has been reported previously.[4]

The parameters plotted were the fractional changes in carrier concentration $f(n)$, and reciprocal mobility $f(1/\mu)$. These parameters were computed as follows:

$$f(n)=(n_0-n_t)/(n_0-n_r),$$

and

$$f(1/\mu)=(1/\mu_0-1/\mu_t)/(1/\mu_0-1/\mu_r).$$

The significance of the subscript is: 0–before irradiation, r–immediately after irradiation, and t–after anneal.

III. EXPERIMENTAL RESULTS

There was no remarkable difference in carrier removal rates between antimony- and arsenic-doped samples. Previous indications[4] that the removal rate was a strong function of impurity concentration were not confirmed. The mean value of the carrier removal rate at 77°K for 15 samples with carrier concentrations in the range

from 5.5×10^{13} cm^{-3} to 5.3×10^{15} cm^{-3} was 6×10^{-4} conduction electrons removed per incident photon.

A typical plot of the changes in carrier concentration and reciprocal mobility for an antimony-doped sample is shown in Fig. 1. The change in carrier concentration is linear throughout the irradiation. The reciprocal mobility is nearly linear until near the end of the irradiation where there is a marked upward curvature.

The fractional change in reciprocal mobility as a function of the fractional change in carrier concentration is shown in Fig. 2 for an arsenic-doped sample and in Fig. 3 for an antimony-doped sample. The difference between the irradiation and annealing curve in the case of As-doped material is well known and was first reported by Brown *et al.*[1] This difference is much less pronounced in the case of Sb-doped material. The value of reciprocal mobility after anneal was less than the preirradiation value in both cases.

The isochronal anneals of four Sb-doped samples are shown in Fig. 4. The impurity concentrations range from 5×10^{13} to 5×10^{15} cm^{-3}. There is an annealing stage which starts at about 100°K (low-temperature stage LT) and reaches a plateau after removing $\sim$5% of the induced change in carrier concentration. After the saturation of this LT stage, there is no further annealing until the sample has been warmed up to about 260°K. There is an anneal in the room-temperature range (RT) which is dependent on the impurity concentration. Another annealing stage occurs in the intermediate temperature range (IT) beginning at about 350°K. This is followed by a high temperature (HT) anneal which sets in above 380°K. There is an anomalous behavior in the anneal of the low impurity concentration sample which exhibits an apparent further decrease in electron concentrations in the low-temperature range and may be related to the observations of Gerasimov and Konovalenko[10] who report annealing of an irradiation-induced donor center well below room temperature. This type of behavior has been observed in several samples with Sb concentrations in the range of 5×10^{13} cm^{-3}.

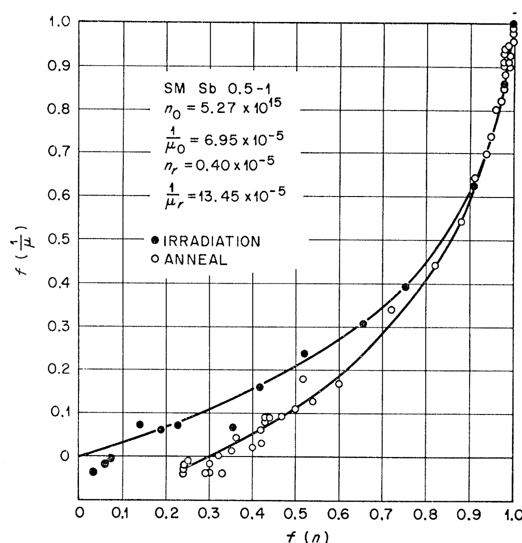

Fig. 3. The relation between the changes in carrier concentration and reciprocal mobility. Antimony concentration 5.27×10^{15}.

The isochronal anneals for three As-doped samples are shown in Fig. 5. There are distinct annealing ranges which can also be designated as low, room, intermediate, and high-temperature ranges. The RT annealing is not so dependent on impurity concentration as is the case in Sb-doped material; however, the plateau after IT anneal does show a marked impurity dependence. The anneal in the low-purity sample saturates with about 70% of the induced change remaining. The corresponding anneal in the sample with 2×10^{14} cm^{-3} saturates with about 50% of the induced change remaining. There is no clear cut plateau in the IT anneal of the high-purity sample. The high-temperature anneal in As-doped material occurs above 420°K, as contrasted with

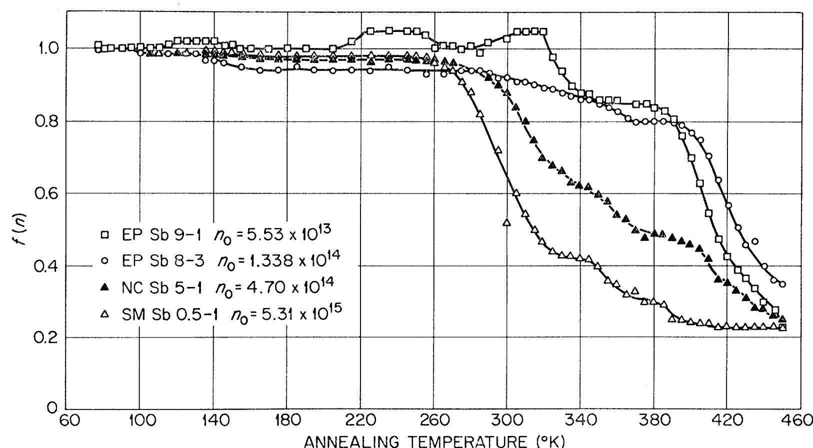

Fig. 4. Anneal of total-state concentration in antimony-doped material.

[10] A. B. Gerasimov and B. M. Konovalenko, Fiz. Tverd. Tela **6**, 3184 (1964) [English transl.: Soviet Phys.—Solid State **6**, 2544 (1965)].

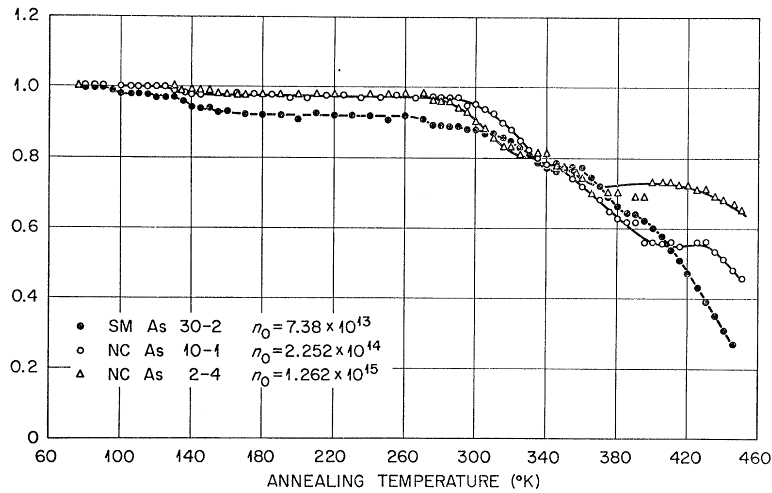

FIG. 5. Anneal of total-state concentration in arsenic-doped material.

380°K for the Sb-doped material in agreement with the observation of Ishino *et al.*[3]

The isochronal anneal of the reciprocal mobility in an As-doped sample is compared with the anneal of the total induced acceptor-state concentration in Fig. 6. The anneal begins immediately even though there is no measurable change in the carrier concentration, and then saturates when the anneal in carrier concentration saturates. There is some structure in the annealing curve of reciprocal mobility at about 220°K for this sample, and there is a further anneal in the RT and IT ranges where mobility saturates at a negative value of $f(1/\mu)$ subsequent to the IT anneal. The annealing curves of reciprocal mobility and total state concentration show similar gross characteristics, but there is structure in each curve which is not reflected in the other.

It is instructive to compare the anneal of the shallow- and deep-state concentrations which can be explicitly separated by means of the Hall-coefficient curves after annealing to 275°K. The anneal of the shallow-, deep-, and total-state concentrations, as well as the reciprocal mobility, in an Sb-doped sample is shown in Fig. 7. The data are normalized to the 275°K value. There is a strong anneal in all parameters which saturates at about 300°K. Another anneal starts at about 350°K. The deep state anneal saturates at about 380°K, but a further anneal sets in at this temperature for the shallow-state concentration and reciprocal mobility. The shallow-state concentration is essentially completely removed by annealing to 450°K, but the deep-state concentration has saturated with about 35% of the induced change remaining. Again the fractional change in the reciprocal mobility saturates at a small, negative value.

The anneal of the shallow-, deep-, and total-state concentrations, as well as the reciprocal mobility, normalized to the 275°K value for an As-doped sample is shown in Fig. 8. The anneal in the deep-state concentration saturates at about 320°K and is followed by a small increase in the deep-state concentration. The deep-state concentration reaches a maximum at about

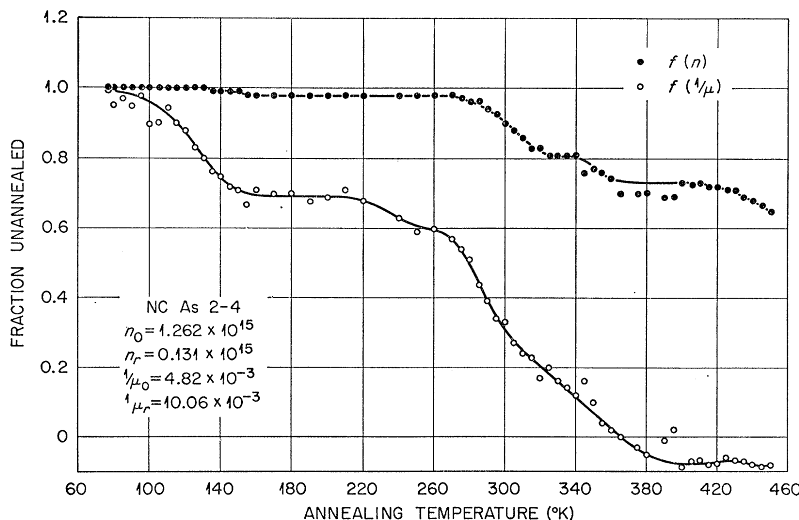

FIG. 6. Anneal of total-state concentration and reciprocal mobility in a sample with an arsenic concentration of 1.26×10^{15}.

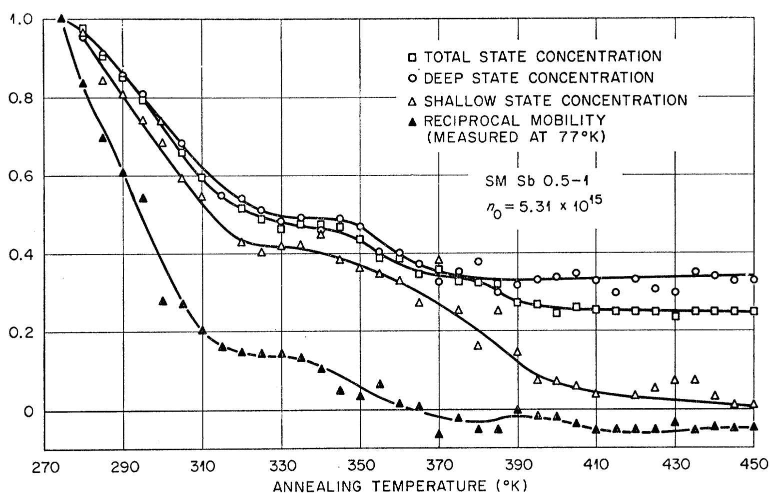

FIG. 7. Comparison of the anneal of shallow-, deep-, and total-state concentrations with the anneal in reciprocal mobility for a sample with an antimony concentration of 5.31×10^{15}.

405°K. The anneal in the shallow-state concentration begins to saturate at about 380°K and shows a shallow minimum at about 405°K. The anneal in the reciprocal mobility shows an inflection in the temperature range at which the saturation in the deep state occurs, but continues to anneal. The reciprocal-mobility anneal saturates when the shallow-state concentration saturates, and the final plateau for the reciprocal mobility is negative, as in the case of the Sb-doped sample.

IV. DISCUSSION

The important aspects of the data which must be considered are the strong influence of the impurity type on the annealing of the electrical properties and the control exerted by the impurity concentration on this annealing behavior. In the following discussion, we will consider first the reciprocal mobility which illuminates one aspect of the irradiation induced defects and their interactions, and, second, the carrier concentration which illuminates another aspect. Finally, we will suggest a speculative model which accounts qualitatively for the various annealing stages and the influence exerted by impurity.

A. Reciprocal Mobility

The linear relationship between the induced change in carrier concentration and irradiation seen in Fig. 1 suggests that there is a constant defect introduction rate for the samples studied. The change in charged scattering-center concentration, as represented by the reciprocal mobility, is also proportional to the integrated photon flux for the early part of the irradiation. One would expect a linear relation between the change in scattering concentration and the ionized-defect concentration. A relation of this type is seen in the early part of the curves of Figs. 2 and 3. The curvature observed near the end of the irradiation can be understood in terms of the Brooks-Herring model for ionized impurity

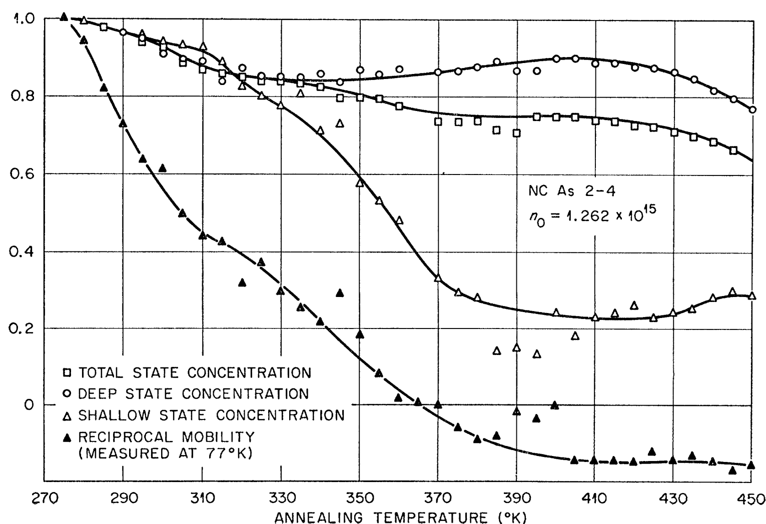

FIG. 8. Comparison of the anneal of shallow-, deep-, and total-state concentrations with the anneal in reciprocal mobility for a sample with an arsenic concentration of 1.262×10^{15}.

scattering.[11] The reciprocal mobility should be proportional to the concentration of charged scattering centers only so long as the screening distance is constant, but the decrease in carrier concentration caused by the irradiation increases the scattering range per center. The concentration of scattering centers toward the end of the irradiation is approximately a factor of 15 larger than the conduction electron concentration. Since the irradiation induced defects may possess more than one acceptor level, these centers may be multi-ionized at 77°K. Approximately 90% of the carriers are removed for the irradiation doses used here. The resulting defects are assumed to be double acceptors. Consequently, these defects constitute $\sim\frac{1}{3}$ of the total concentration of charged scattering centers. The increase in effective scattering per center as the screening is reduced and as multiply charged centers are introduced would require an upward curvature in the $f(1/\mu)$ curve, as occurs in Fig. 1, and an upward curvature in the $f(1/\mu)$- versus-$f(n)$ plots in Figs. 2 and 3.

If the annealing process were to consist of direct annihilation of the irradiation induced defects, one would expect the annealing curves in Figs. 2 and 3 to lie along the irradiation curve. If, on the other hand, the annealing process involves the pairing of centers of opposite charge, one would then expect the annealing curve to deviate from the irradiation curve since the pairing of opposite charges would reduce the carrier scattering without necessarily restoring the measured change in carrier concentration. An effect of this type is evident in Figs. 2 and 3. The reciprocal mobility after the anneal to higher temperature is less than the pre-irradiation value, indicating that in these cases some pairing of defects with impurities or imperfections of opposite sign, or a redistribution of impurities over lattice sites has occurred.

Therefore, it is evident that a comparison of mobility- and carrier-concentration behavior can give a clue to the nature of the underlying kinetic process. Recovery of both of these properties indicates removal of both electronic states and charge centers thereby suggesting defect annihilation, whereas recovery in mobility only indicates defect rearrangement.

B. Influence of Impurity

The dependence of annealing on impurity type is perhaps best illustrated by comparison of Figs. 7 and 8. We shall discuss the details of the two sets of data separately. Since we wish to compare the effect of impurity type, a comparison is made between the samples which have the highest arsenic and antimony concentrations to accentuate this difference. This is done in Figs. 7 and 8.

1. Antimony

The deep- and shallow-state concentrations, as well as the reciprocal mobility (shown in Fig. 7), anneal together in the temperature range from 275 to 380°K, indicating that the annealing results in the removal of defects. The annealing is not a simple process because there are two definite annealing stages in this temperature range which are separated by a plateau. Annealing above 380°K is characterized by removal of the shallow-state concentration without changing the deep-state concentration. The reciprocal mobility indicates an annealing behavior parallel to that of the shallow-state concentration.

This behavior suggests that there is a process which involves an easy defect destruction occurring in the room-temperature range. The amount of annealing which takes place by this process is controlled by the antimony concentration. There is a residual fraction of the damage, larger for smaller antimony concentrations, which anneals at a higher temperature by some sort of defect rearranging process, leading to a different distribution of defect states rather than simple defect annihilation.

2. Arsenic

Except for the reciprocal mobility, the arsenic-doped sample shown in Fig. 8 exhibits little annealing occurring in the RT range. This is in marked contrast to the behavior of the antimony sample, as seen in Fig. 7. The dominant process for the arsenic-doped sample is clearly removal of the shallow state concentration. In fact, there is some increase in the deep state concentration in the IT range.

C. A Possible Model

1. The Nature of the Defects

Any interpretation of the annealing of the macroscopic properties is highly speculative in the absence of microscopic information about the identity of the defects. Nevertheless, it is instructive to examine the types of processes which may be responsible for the recovery occurring in the different temperature ranges and which are influenced by impurity type or concentration. In the absence of detailed microscopic information, we are forced to rely upon analogy with the irradiation-induced defects and complexes resulting from subsequent defect motion which have been observed in silicon. The chemical and structural similarity of the homologues germanium and silicon leads one to expect that complexes of the type found in silicon also may be important in irradiated germanium. The formation or decomposition of these complexes would be seen as annealing stages. We will not be concerned in our discussion with recombination of close interstitial vacancy pairs. This problem has been extensively investigated by MacKay *et al.*[12,13]

[11] P. B. Debye and E. M. Conwell, Phys. Rev. **93**, 639 (1954).

[12] J. W. MacKay and E. E. Klontz, in *7th International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1965), Vol. 3, pp. 11–26.

[13] T. A. Callcott and J. W. MacKay, in *7th International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1965), Vol. 3, pp. 27–33.

There is no evidence that the irradiation-produced interstitial in germanium or silicon is stable at temperatures as high as 77°K. It has been suggested that the interstitial might move as an interstitialcy and become trapped by replacing an impurity atom.[14] The interstitialcy chain is then broken and the process becomes one of interstitial diffusion of the resultant interstitial impurity. The smallest known interstitial ion in a germanium lattice is lithium, which moves with an activation energy of 0.51 eV.[15] One would then expect the much larger interstitial arsenic or antimony to have a motion energy greater than this value and to be virtually immobile at least up to room temperature. A mechanism of this type could account for the observation of Watkins[9] that interstitial aluminum atoms and isolated vacancies are present in approximately equal concentrations in aluminum-doped silicon, which has been irradiated at 4°K.[5] The aluminum interstitial is stable up to ~200°C. It is reasonable then to postulate that the defects resulting from ^{60}Co gamma irradiation of germanium at 77°K consists primarily of vacancies and interstitial-impurity atoms. It is probable that a small number of divacancies may also be produced by the irradiation since these have been observed as a primary defect in irradiated silicon.[16]

If the interstitial germanium is so highly mobile, one might expect that it would recombine with its associated vacancy, or some other vacancy. In such a case, there would be competition between the vacancies and impurity atoms for the mobile germanium interstitialcy, which would lead to an introduction rate dependent on the relative concentration of vacancies and impurity atoms. Therefore, the defect introduction rate should vary during the irradiation. In all of our irradiations, however, the introduction of defects is linear. MacKay and Klontz present evidence[17] that there is a critical separation of the Frenkel defect-close pair beyond which there is a barrier to direct recombination. Therefore, one may conclude that, in the range where the interstitials are unable to surmount this barrier, those interstitials which are not trapped in the form of interstitial impurities will escape to surfaces or dislocation sinks. According to this view, the yield of defects during irradiation would not be appreciably sensitive to the impurity content.

The germanium interstitial produced by the primary event can migrate through the crystal at the temperature of the irradiation; it can go to a surface or jog on a dislocation line and be lost, or it can produce an interstitial impurity. The probability of interaction with an impurity atom will be proportional to the concentration of impurity atoms and the cross section for the interaction—the latter depending upon the identity of the impurity. Consequently, the radiation-induced defects with more than a transitory existence for irradiation temperatures where the vacancies are immobile consist of vacancies, divacancies, and interstitial impurity atoms. Although we have no assurance on this point, it seems reasonable to assume that the interstitial donor is singly ionized. If the interstitial donor atoms were doubly ionized, as has been observed in the case of acceptor atoms, there is a high probability that in silicon they would have been detected by the spin-resonance measurements by Watkins. The change in carrier concentration would then be proportional to the concentration of vacancies plus a smaller contribution from the divacancies. A corresponding change in reciprocal mobility would occur as discussed above. If, on the other hand, the vacancies are mobile at the irradiation temperature, then they will exist in some trapped state. The observed change in carrier concentration at liquid-nitrogen temperature would then be due to these trapped vacancies.

2. *Annealing Processes*

The various possible processes will be discussed, first, in terms of their expected effect on the measured properties, and, second, in terms of the annealing curves.

(a) Vacancies may migrate to surfaces or jogs in dislocation lines and be lost. The loss of such vacancies would produce a change in carrier concentration and charged-scattering-center concentration, thereby affecting both n and $1/\mu$.

(b) Migrating vacancies may be captured by either substitutional or interstitial donor atoms. In the first case, a vacancy-substitutional impurity complex would be formed. Such centers have been identified by spin resonance in silicon.[9] In the second case, annihilation of the vacancy by the interstitial impurity can occur provided that there is no barrier to recombination. It seems reasonable to postulate that a barrier does exist since it has been necessary to postulate such a barrier between a germanium interstitial and a vacancy. Therefore, a loosely bound complex may also result here. In both cases, complex formation would reduce the effective scattering of carriers, and also might alter the defect acceptor level structure. An alteration of the defect level structure would be reflected in the temperature dependence of the Hall curve.

(c) Vacancies trapped by interstitial impurities, as postulated above, can be annihilated provided the barrier can be surmounted, resulting in a substitutional impurity. Such a process would have an activation energy which is dependent on the type of impurity involved. The annihilation of the vacancy would result in a recovery in both n and $1/\mu$ by a first-order process.

(d) The vacancy-substitutional impurity can break up, releasing a vacancy back to the lattice. Once again

[14] J. H. Crawford, Jr., in *The Interaction of Irradiation with Solids*, edited by R. Strumane, J. Nihoul, R. Gevers, and S. Amelinckx (North-Holland Publishing Company, Amsterdam, 1964), pp. 421–470.

[15] C. S. Fuller and J. C. Severiens, Phys. Rev. **96**, 21 (1954).

[16] G. D. Watkins and J. W. Corbett, Phys. Rev. **138**, A543 (1965).

[17] J. W. MacKay and E. E. Klontz, J. Appl. Phys. **30**, 1269 (1956).

the activation energy for the process would be dependent on the type of impurity. The effect of the break up of the complex would be determined by the eventual fate of the resulting free vacancy. If the binding energy is large compared to the energy of vacancy motion, the anneal would reflect the former as the activation energy.

(e) Vacancies may migrate to vacancy-impurity complexes and produce a divacancy-impurity complex. The presence of the positively charged donor would relax the Coulomb repulsion which might otherwise prevent divacancy formation. The binding energy of the complex, by analogy with the findings of Watkins and Corbett[18] for a divacancy in silicon, would be expected to be rather high. Watkins[9] also finds a different energy-level structure for the vacancy and divacancy. There are fewer total acceptor states available for the divacancy than for two isolated vacancies. In the case of germanium, previous work suggested that the vacancy has one shallow and one deep state, where the impurity-divacancy complex has two deep states and no shallow state. Hence, the formation of such a complex would decrease the shallow state concentration but not the deep state concentration.

(f) Interstitial impurity motion must also be considered. An interstitial impurity may diffuse to a vacancy-impurity or an impurity-divacancy and either be trapped as an interstitial or annihilated at a vacancy. If the interstitial were trapped, one would expect a change in $1/\mu$ but not necessarily in n, but if the interstitial annihilated a vacancy in the complex, one would expect a change in n and $1/\mu$.

(g) The interstitial may diffuse to a substitutional impurity and be trapped. Such interstitial-substitutional impurity pairs have been observed in gallium-doped silicon.[9] However, in view of the fact that both the substitutional and interstitial donor impurities are positively charged, the likelihood of this process is considered to be slight.

3. *Anneal of Antimony-Doped Material*

Whether processes 1 and 2 above are observed depends upon whether vacancies are mobile at the irradiation temperature. In studies of oxygen-doped germanium, Whan[19] has observed the formation of some oxygen-defect interaction product at $\sim$65°K after electron bombardment at 25°K by infrared-absorption measurements. A further modification in the infrared spectrum occurs near 120°K. Whan interprets the 65°K process as vacancy motion resulting in vacancies being trapped by oxygen atoms, and the second process as rearrangement of the oxygen-vacancy complex. If this interpretation is valid, one would expect that there would be no free vacancies remaining in our specimens after liquid-nitrogen irradiation. On the other hand, if the 120°K process is due to vacancy motion, we would expect to see a relaxation in the same temperature range. However, the fact that we do observe an annealing stage at 120°K is not conclusive evidence that vacancy motion occurs here since vacancies held in shallow traps may be released at this temperature. If the 120°K annealing stage is due to vacancy motion, we would expect to see $1/\mu$ and n anneal differently. However, they recover together, suggesting that this stage is the result of annihilation of some sort of trapped vacancy.

For the purpose of this discussion, we will assume with Whan that vacancy motion has occurred during the irradiation and that the vacancies remaining in the sample are trapped by interstitial impurities, substitutional impurities, or by the strain field around dislocation lines. The number of vacancies trapped by dislocation lines because of the typically low dislocation density of these crystals would be small, but their subsequent anneal could produce a measurable change in $f(1/\mu)$ due to the very strong dependence of scattering power on carrier concentration, even though the change in $f(n)$ may be below the threshold of detection. This anneal removes less than 10% of the induced change in carrier concentration and does not depend upon donor impurity type or concentration. Both $f(n)$ and $f(1/\mu)$ anneal in this range, which indicates vacancy annihilation. The 120°K anneal may be attributed to the annihilation of vacancies upon their release from dislocation lines or escape from some other unidentified shallow traps. A similar annealing stage has been observed by Wikner[20] who employed 3–45-MeV electron irradiation. The fractional recovery he observers at 120°K is much greater than that observed here. This may be associated with the fact that the configuration of the damage resulting from high-energy electron irradiation is different from the damage resulting from ^{60}Co gamma irradiation. Such an extensive annealing as observed by Wikner suggests large-scale motion of defects, but there is no striking disparity between the recovery of $1/\mu$ and n as would be expected if vacancy complexes were being formed. This suggests that defect annealing rather than complex formation occurs in the 120°K anneal. It is difficult to tell from this evidence whether or not vacancies are moving at or below 120°K. Additional study is needed on this point.

There is no further anneal until the RT range is reached. This is additional evidence that all the remaining vacancies are trapped. The trapping of the vacancies can be accounted for in terms of the formation of vacancy-interstitial impurity and vacancy-substitutional impurity complexes.

Annealing is resumed when the temperature reaches the RT range. Since both deep and shallow states and

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[19] R. E. Whan, Appl. Phys. Letters **6**, 221 (1965).
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mobility anneal, as can be seen in Fig. 7, this stage is quite probably associated with defect removal. The extent of room-temperature recovery is strongly dependent on impurity concentration, as shown in Fig. 4. There are two processes which might account for the impurity-concentration-dependent annealing: Anneal of vacancies trapped at the impurity interstitial by a thermally activated recombination to form a substitutional impurity, and migration of interstitial impurities to trapped vacancies. In either case all parameters would recover together. The relaxation time in the first instance would be governed by a frequency factor near atomic vibration frequency and the height of the barrier separating the trapped vacancy from the impurity, but in the second case it would depend both on the rate of motion of the interstitial impurity and the concentration of the species with which it interacts. In the first case, first order kinetics is expected whereas in the second it would be second order or pseudo first order. This evidently is the process investigated by Brown *et al.*[1] which occurred with an activation energy of 0.8 eV and could not be fit by a first-order process. Although an analysis of our data suggests first order recovery, isochronal annealing is not so precise a way for such a determination. The relaxation times observed by Brown *et al.* are sufficiently long for a defect moving with this activation energy to make 10^4 jumps. Therefore, transportation over long distances may be involved in this process. Unfortunately, recovery in the RT range is so extensive that previous information resulting from room-temperature irradiation is not applicable to this point.

As the annealing temperature is increased, the point is reached in the IT range at which the thermal energy available approaches the binding energy of the vacancy-substitutional impurity complex. The complex breaks up and the vacancy diffuses through the lattice. The vacancy may go to surfaces or dislocation lines and be lost; it may go to a remaining interstitial impurity and be annihilated; or it may interact with a vacancy-impurity pair and form a divacancy-impurity complex. From analogy with silicon, the binding energy of the divacancy complex is expected to be quite high. Thus the divacancy-impurity complex which is further stabilized by the positive charge of the donor would be quite stable.

Our information is not extensive in the HT range. The annealing in this range probably results from breakup of remaining complexes, as discussed by Ishino *et al.*[3]

The first two of these processes will produce an anneal in all parameters. The third process will cause an anneal in the shallow-state concentration but not in the deep-state concentration (see above). An effect of this type is evident in Fig. 7. This IT range has been studied in detail[4] for antimony-doped material with an impurity concentration of the order of 1.4×10^{14} cm^{-3}.

5. *Anneal of Arsenic-Doped Material*

The room-temperature anneal in the arsenic-doped sample removes very few defects. The dominant annealing stage is in the IT range in which defect rearrangement occurs. If the cross section for interstitial germanium impurity interaction were much smaller for arsenic than for antimony, there would be fewer interstitial impurities formed during irradiation; hence, a much smaller contribution of vacancy-interstitial impurity annihilation would be present in the RT range. Consequently, there would be only a small anneal in this stage. Conversely, the higher concentration of vacancy-substitutional impurity complexes would increase the probability of formation of divacancy-impurity complexes. Evidence of an effect of this type can be seen in Fig. 8.

Since vacancies which have been released from vacancy-impurity complexes can also be lost to dislocation lines or surfaces, the fraction that is captured to form the divacancy-impurity complexes will be greater for higher concentrations of vacancy-substitutional impurity complexes. Hence, there will be a higher plateau after the room-temperature anneal for samples with higher impurity concentration. An effect of this type is seen in Fig. 5. The sample with the lowest arsenic concentration shows no plateau at all. An analysis of the deep- and shallow-state concentrations for this sample shows that all parameters anneal together, which is in accord with the above model.

V. CONCLUSION

The annealing of Sb- and As-doped germanium below room temperature is not strongly dependent on the type or concentration of the impurity present. Above 270°K, however, the annealing is strongly dependent on impurity type and concentration. The extent of recovery of damage in Sb-doped samples increases in the RT range with increasing Sb concentration. This annealing is attributed to defect removal by mutual annihilation of interstitial impurities and vacancies. The annealing of As-doped samples in the RT range is not extensive, but at a higher temperature (IR range) it is dominated by a process which rearranges the defects in the more highly doped samples. However, the samples with a low-arsenic-concentration anneal by defect removal.

In this paper we have proposed a logically consistent model to account for the annealing behavior of antimony- and arsenic-doped germanium that has been irradiated with ^{60}Co gamma rays. The model accounts for the influence of impurity type and concentration in terms of defect-impurity interaction which might be expected by analogy with silicon. We emphasize again that the model is highly speculative and that its main virtue is in demonstrating how one might understand such diverse behavioral dependence on impurity type and concentration.