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Annealing of Defects Produced in *n*-Type Ge by Electron Irradiation at 30°K*

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Attention is focused upon a primary radiation defect in *n*-type germanium created by 1.5-MeV electron bombardment at 30°K. This defect anneals in a stage centered near 150°K but is not present when specimens are exposed at 10°K to 0.7-MeV electrons or at 77°K to either 1.0-MeV electrons or ^{60}Co γ rays. The 150°K stage can be shifted to lower temperatures under the influence of white light and, presumably, ionizing radiation. The characteristics of this defect are similar to those found by Vook and Stein for the so-called irradiation-temperature-independent defects produced by electron bombardment of *n*-type silicon in the temperature range 77–150°K. Therefore, we adopt the same model as they, namely, that the defect responsible for the 150°K annealing stage is a nonreorientable divacancy anchored in a fixed orientation by an interstitial nearby (I-V_2 defects). From this experiment it can be concluded that the principal defects introduced by irradiation below 65°K with electrons less than 1 MeV are close pairs which anneal in a stage centered near 65°K, whereas irradiation with electrons of energy greater than 1 MeV introduces I-V_2 defects also.

I. INTRODUCTION

ELECTRICAL property measurements by MacKay and Klontz[1] of the annealing of lattice defects introduced in degenerate *n*-type Ge by 1.1-MeV electron irradiation at 10°K have revealed a major annealing stage at or below 65°K, and another type of lattice defect stable at least to 80°K. A model of close pairs was proposed that provides a reasonable interpretation for the strong dependence of the defect introduction rate on the type of carrier and amount of impurity, and for the annealing behavior induced by illumination at low temperature; however, the model does not provide an explanation for the creation of the so-called "permanent defects" that anneal above 80°K.

Annealing measurements in the same temperature range have been made by Callcott and MacKay[2] following 0.7- and 4.5-MeV electron irradiation of *n*-type Ge with a wide range of donor concentrations at 4.2°K. Approximately 95% of the conductivity change produced by 0.7-MeV electron irradiation was attributed to close pairs and annealed at 65°K, whereas only 50% of the conductivity change produced by 4.5-MeV electron irradiation annealed at 65°K, and the remainder was stable after annealing at 90°K. Brown *et al.*[3] used 1.0-MeV electrons and Saito *et al.*[4] used 1.25-MeV ^{60}Co photons to irradiate *n*-type Ge at 77°K, and here the permanent defects were stable against annealing to nearly room temperature, whereas Wikner[5] irradiated *n*-type Ge at 80°K with 5–45-MeV electrons and observed a significant amount of annealing between 80 and 300°K. More recently, the present authors[6,7] have shown that electron irradiation at 77°K of *n*-type Ge doped with Cu or Sb produces interstitial atoms of Cu or Sb through an interaction of the mobile interstitial Ge and the substitutional Cu or Sb, and the subsequent annealing in the range 77–250°K was attributed to the recombination of isolated vacancies with interstitial atoms of Cu or Sb.

Ishino and Mitchell[8] have shown that the annealing temperature of the 65°K stage introduced by 2.0-MeV electron irradiation of *n*-type Ge at 10°K is lowered as a consequence of illuminating the specimen, and Zizine[9] has shown that illumination at 35°K of specimens irradiated with 1.5-MeV electrons at 20°K served to remove the permanent defects that had been observed to anneal near room temperature. More recently, Werner *et al.*[10] have irradiated *n*-type Ge with 2.0-MeV electrons at 10°K, and have suggested that a dominant damage center is the interstitial Ge atom, that it can exist in three possible charge states (for instance, −1, 0, 1), and that the interstitials in *n*-type Ge are unstable with respect to a change in their charge state at around 30°K.

It is evident that the effect of illumination is not simply a shift of the annealing temperature, and that some correlation must exist between the close-pair model, the permanent defects produced at low temperatures, and the impurity-dependent defects produced at higher temperatures. The purpose of this paper is to

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report our efforts[11] to identify the type of defects created in *n*-type Ge as a consequence of 1.5-MeV electron irradiation at 30°K.

II. EXPERIMENTAL PROCEDURE

Antimony- and arsenic-doped *n*-type single-crystal specimens were cut from 0.5-mm ingot slices as bridge-type samples for Hall-coefficient and resistivity measurements. Single-crystal specimens were also prepared from an ingot section containing 4.5×10^{15} Sb donors cm^{-3}, and Cu was diffused into these specimens by conventional procedures in a nitrogen atmosphere. The diffusion temperature (675°C) was selected to provide a ratio of Cu to Sb of $\sim1:4$, and the specimens were annealed at 300°C for 10 h to remove any interstitial Cu. The final concentration was $\sim1.1\times10^{15}$ Cu atoms cm^{-3}. The specimens were mounted in a liquid-helium cryostat which permitted a total irradiation time of more than 30 min at an average current density of 0.5 $\mu\text{A/cm}^2$ of 1.5-MeV electrons at a specimen temperature of 30°K. The magnetic-field strength for Hall-coefficient measurements was 4000 G, and the current through the specimen was limited to 0.1 mA. All of the irradiations were performed in such a manner that the total number of carriers removed was $\sim90\%$ of the initial concentration at 50°K, as determined by Hall-coefficient measurements subsequent to the irradiation. The samples were then annealed at 65 and 77°K to remove the 65°K defect stage, and the amount of this annealing was determined by Hall-coefficient measurements at 50°K. Isochronal anneals of 30-min intervals were then conducted at each of several temperatures between 77 and 375°K, and the fractional recovery was determined by electrical measurements after each anneal. The anneals were conducted either in the dark or under illumination as provided by a small tungsten filament lamp (5 V dc, 0.06 W) that was installed in the specimen chamber of the cryostat.

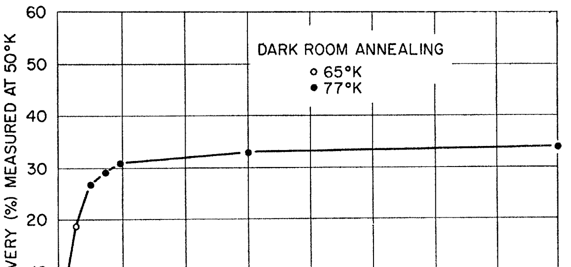

FIG. 1. Recovery of the initial carrier concentration (%) measured at 50°K versus the total annealing time (h) at 65 and 77°K for a sample of Ge irradiated at 30°K with 1.5-MeV electrons.

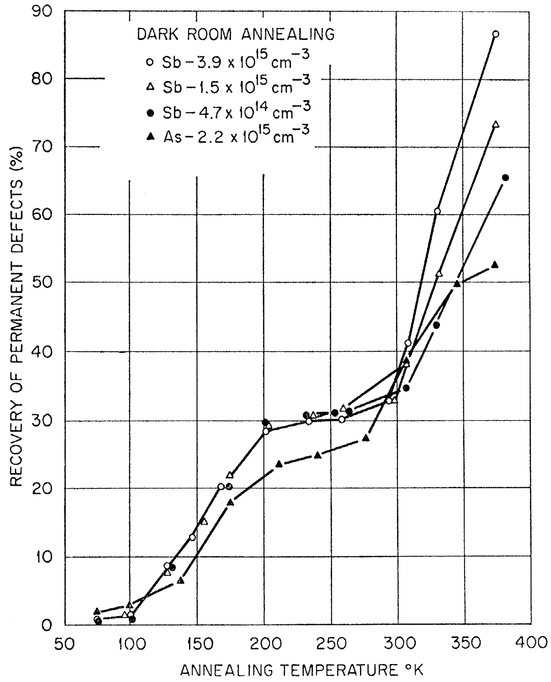

FIG. 2. Recovery of permanent defects (%) versus the annealing temperature (°K) for Sb- or As-doped *n*-type samples of Ge after irradiation at 30°K and annealing at 77°K.

III. RESULTS

Figure 1, which is a graph of the recovery of the initial carrier concentration (%) measured at 50°K versus the total annealing time (h), indicates that 5–10 h at 77°K were sufficient to remove all of the 65°K defects. The ratio of 65°K defects to "permanent defects" was 35–65% for all of the samples irradiated at 30°K. The samples were kept at 77°K for ~16 h before starting the isochronal anneals.

A. Isochronal Anneal of Permanent Defects in the Dark

Figure 2, which is a graph of the recovery of permanent defects (%) versus the annealing temperature °K, shows data for three Sb-doped and one As-doped specimen, and indicates a defect-annealing stage around 150°K. This annealing stage, which represents about 30% of the total recovery, was not observed in previous experiments involving 1.0-MeV electron[3] or 1.25-MeV ^{60}Co photon[4] irradiation of *n*-type Ge at 77°K, but some indication of this stage was observed by Zizine[9] following 1.5-MeV electron irradiation of *n*-type Ge at 20°K. Also shown is a second stage located near room temperature. The annealing characteristics of this second stage are very similar to those observed following electron[3] or ^{60}Co photon[4] irradiation at 77°K in that recovery is dependent upon the type and concentration of impurity; however, there was no indication of an impurity type or concentration dependence for the annealing stage around 150°K.

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B. Isochronal Anneal of Permanent Defects under Illumination

The fact that no type of annealing stage was observed around 150°K following irradiation by 1.0-MeV electrons[3] or 1.25-MeV ^{60}Co photons[4] at 77°K might suggest that this lower energy of irradiation generates a sufficient number of ionizing events (electron-hole pairs) during irradiation to alter the charge state of the defects sufficiently to permit lower temperature annealing. It was therefore decided to repeat the annealing studies with the sample under some type of ionizing radiation. A small tungsten-filament lamp was selected for this purpose. The light was not filtered, hence most of the electron-hole pairs were generated near the surface; however, the thin sample (0.5 mm), long illumination time (30 min), and relatively large diffusion length of the excess carriers should have permitted a reasonably homogeneous distribution throughout the specimen.

The treatment of the samples for this part of the study was identical up to the point of illumination in that they were irradiated at 30°K and annealed in the dark at 65 and 77°K for ~16 h. Figure 3, which is a graph of the recovery of permanent defects (%) versus the annealing time in minutes, shows that no annealing occurred in the dark; however, a 10% recovery was observed at 77°K under illumination. Warming the sample to 100°K in the dark had no further effect; however, there was an additional 10% recovery under illumination at 100°K.

It is evident that illumination at 77 or 100°K serves to facilitate the anneal or removal of permanent defects, whereas no such behavior was observed at these temperatures in the dark. Figure 4, which is a graph of the recovery of permanent defects (%) versus the annealing temperature °K, shows typical data for one Sb-doped and one As-doped specimen under illumination, and one Sb-doped specimen as annealed in the dark. It is evident that the dark-annealing stage located near 150°K has been shifted to a much lower temperature as a consequence of illumination, and no particular dependence on the type or concentration of chemical dopant is observed. The stage near room temperature, however, was not affected by illumination, and the annealing data are very similar to those obtained in the dark.

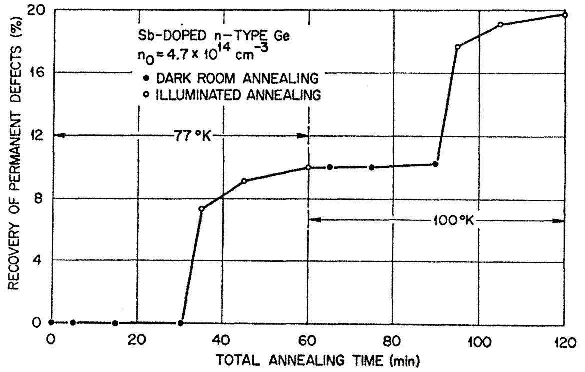

FIG. 3. Recovery of permanent defects (%) versus the total annealing time (min) for an Sb-doped *n*-type sample of Ge illuminated at 77 and 100°K.

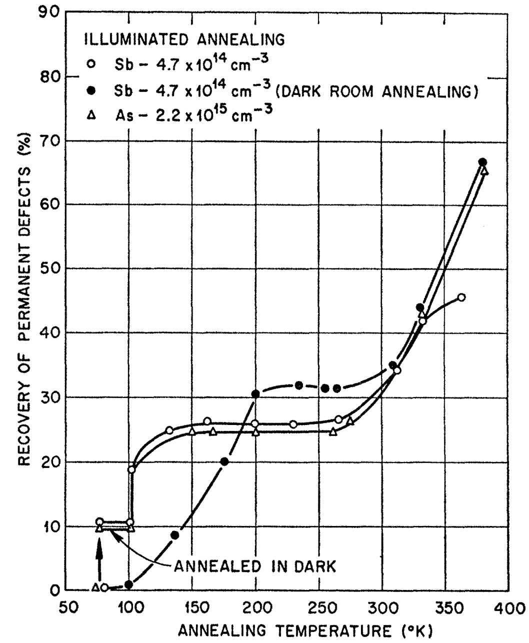

FIG. 4. Recovery of permanent defects (%) versus the annealing temperature (°K) for Sb- or As-doped *n*-type samples of Ge when illuminated, as compared with an Sb-doped specimen annealed under darkroom conditions.

C. Isochronal Anneal of Cu-Doped *n*-Type Ge

To study the recovery in *n*-type Ge containing Cu, specimens again were irradiated at 30°K with 1.5-MeV electrons until ~90% of the initial carriers had been removed. They were then annealed at 65 and 77°K in the dark.

Figure 5, which is a graph of the recovery of permanent defects (%) versus the annealing temperature °K, shows typical data for one Cu-doped *n*-type specimen annealed under darkroom conditions and a similar specimen annealed under illumination. The data for the Sb-doped specimen are also shown for comparison. It is evident that the apparent amount of recovery of permanent defects is less at low temperatures for the samples containing both Cu and Sb impurities, and that the annealing stage near 150°K was shifted to a lower temperature by illumination; however, the annealing of the defect stage near room temperature was not affected by the illumination.

D. Photoresponse of *n*-Type Ge

Previous experiments[6] have shown that Cu-doped *n*-type Ge exhibited a pronounced positive photoconductivity (increase in carrier concentration) when illuminated at 77°K before irradiation, and that

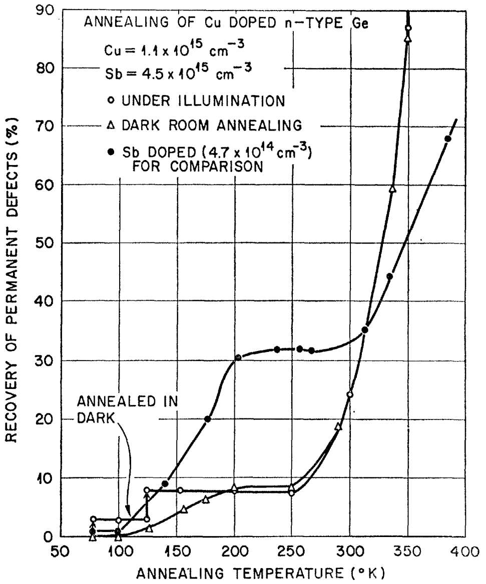

FIG. 5. Recovery of permanent defects (%) versus the annealing temperature (°K) for Cu-doped *n*-type Ge under darkroom and illuminated annealing, as compared with an Sb-doped specimen annealed under darkroom conditions.

illumination following 1.6-MeV electron irradiation at 77°K induced a negative photoconductivity. Figure 6, which is a graph of the photoresponse (change in electron concentration) at 77°K for several samples, demonstrates this same negative photoconductivity following irradiation at 77°K; however, those samples of *n*-type Ge that contained Sb or Cu and Sb impurities that were irradiated at 30°K and annealed at 77°K showed a positive photoconductivity (increase in carrier concentration) when illuminated at 77°K.

IV. DISCUSSION

The minimum electron energy required to displace a lattice atom in Ge is about 0.4 MeV, and the average energy transfer from a 1.0-MeV electron to a lattice atom is about 13 eV. One would therefore expect that the primary result of the 0.7-MeV electron irradiation of *n*-type Ge at 4.2°K by Callcott and MacKay[2] would be the displacement of a single lattice atom, and the creation of near-neighbor or close-pair-type defects. The fact that 95% of the initial change in conductivity annealed at 65°K would suggest that the components of the pair are not very mobile at 4.2°K, and do not tend to separate. Hence a recombination of near-neighbor pair-type defects is the primary annealing process.

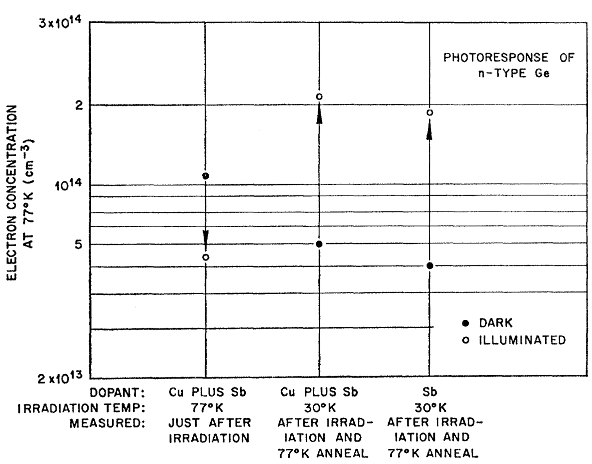

FIG. 6. The photoresponse of Cu-doped *n*-type Ge after irradiation at 77°K, as compared with the photoresponse of Cu- or Sb-doped Ge after irradiation at 30°K and annealing at 77°K.

The average energy transfer for a 5.0-MeV electron is about 94 eV, a value some seven or eight times that required to displace a Ge atom. Only ~50% of the conductivity change observed by Callcott and MacKay[2] to result from 4.5-MeV electron irradiation of *n*-type Ge at 4.2°K can be recovered upon annealing at 65°K, and this annealing is evidently due to the same type of primary defect as was responsible for recovery in the 0.7-MeV electron irradiation. A second type of primary defect is distinguished by the fact that it is still present after annealing to 90°K. The dependence of the introduction rate of this defect on bombardment energy strongly suggests that it is associated in some way with a multiple displacement. One possibility is some form of a double vacancy. We shall refer to this as a multicenter defect.

In the present experiments, the use of 1.5-MeV electrons and an irradiation temperature of 30°K might be expected to produce close pairs and multicenter defects. In previous work we have shown[6,7] that 1.6-MeV electron irradiation of *n*-type Ge at 77°K produces interstitial chemical impurities through an interaction between mobile interstitial Ge displaced by irradiation and the substitutional chemical impurity, and the subsequent annealing near room temperature was attributed to the recombination of these interstitial impurities with vacancies since the latter are released from some type of trap. Therefore, in addition to close pairs and multicenter defects, one might expect some isolated interstitials and vacancies to be produced at 30°K as well.

We must now inquire about the process responsible for the 150°K stage. The close pairs evidently anneal at 65 and 77°K in the dark, and the interstitial Ge is expected to have changed places with Sb or Cu long before 150°K is reached. Hence the 150°K stage might be due either to the capture of vacancies by substitutional and/or interstitial impurity, or some process associated with the multicenter defect. If vacancy annihilation at interstitial impurity were involved, one would expect a reverse annealing, or a further decrease in apparent electron concentration for Cu-doped Ge in this temperature range.[6] However, the data of Fig. 5 indicate that the fractional recovery of permanent defects was less for the Cu-doped than for the Sb-doped samples, which would not be the case if the primary mechanism were that of restoring an interstitial Cu donor to a lattice site where it acts as a triple acceptor. Therefore, the 150°K stage appears to be associated with some process involving the multicenter defect.

In many respects the multicenter defect responsible for the 150°K stage resembles the irradiation-temperature-independent (ITI) defects studied by Vook and Stein,[12] and by Gregory and Barnes.[13] For example, both are favored by the higher bombardment energies and both are unstable in the presence of excess holes introduced by ionizing radiation. The ITI defect is attributed to a "nonreorientable" divacancy which, following Watkins,[14] is described as a divacancy anchored in a given orientation by an interstitial trapped nearby (I-V_2). We conclude that the same type of multicenter defect is present in *n*-type Ge exposed to 1.5-MeV electrons at 30°K, since there was no indication of an impurity type or concentration dependence for the annealing stage around 150°K. It would appear, therefore, that the 150°K annealing stage results when the trapped interstitial surmounts the barrier separating it from the divacancy, annihilates one member of the pair, and thereby releases the second vacancy to migrate to a vacancy trap.

The so-called permanent defects observed by MacKay and Klontz,[1] Brown *et al.*,[3] and Saito *et al.*[4] are presumably isolated vacancies and interstitial chemical impurities that are stable against annealing to nearly room temperature. Presumably the irradiation conditions (energy of incident radiation, charge density, etc.) were such that I-V_2 either were not formed or were unstable. On the other hand, Callcott and MacKay[2] and Wikner[5] would have produced I-V_2 defects with 4.5–5.0-MeV electrons, and Wikner[5] actually observed a significant amount of annealing near 150°K.

The question to be faced next is: How are these defects rendered unstable by ionization? Callcott and MacKay[2] have suggested that the form of the close pair that is stable to 65°K bears one negative charge and is rendered unstable, i.e., recombines, upon loss of another electron by thermal ionization or by irradiation with subthreshold electrons. This conclusion is also in accord with the one reached by MacKay and Klontz[1] on degenerate *n*-type specimens.

Taking our cue from Callcott and MacKay,[2] we shall adopt a simple atomistic model of the I-V_2 defect to account for its instability under ionizing conditions. $(I\text{-}V_2)_1 = I^0 - V_2^=$, the stable configuration, and $(I\text{-}V_2)_2 = I^+ - V_2^=$, the unstable configuration. The $(I\text{-}V_2)_1$ configuration is expected to be prevalent at the initial temperature of formation (4.2–30°K). Thermal ionization, irradiation with subthreshold electrons, or illumination would be expected to favor loss of an electron to the conduction band, thereby enhancing the recovery of permanent defects at temperatures well below those at which the thermal process occurs.

A decrease in electron concentration, or negative photoconductivity, was observed at 77°K for Cu-doped samples that were irradiated at 77°K, and the origin of the negative photoconductivity was attributed to the presence of interstitial Cu impurity atoms.[6] These samples did not contain (I-V_2)-type defects, and the reverse annealing (further decrease in electron concentration) on annealing was attributed to the restoration of interstitial donor Cu to substitutional acceptor type. The apparent increase in electron concentration, or positive photoconductivity, that was observed in both the Sb-doped and Sb-plus-Cu-doped specimens (Fig. 6) after irradiation at 30°K and annealing at 77°K, may reflect the presence of (I-V_2)-type defects in these samples, and the absence of reverse annealing between 77 and 250°K (Fig. 5), may indicate that the process involving the breakup of the (I-V_2)-type defect is more pronounced in this temperature range than that involving the interstitial impurities.

V. CONCLUSION

The primary effect of low-energy (<1.0 MeV) electron irradiation below 65°K is the creation of a close-pair defect that anneals near 65°K, or at lower temperatures under illumination or subthreshold ionizing radiation. Moderate-energy (1–5 MeV) electron irradiation below 65°K can produce close pairs and nonreorientable divacancies, presumably as a consequence of multiple displacements. This latter defect appears to be formed as an $I^0 - V_2^=$ structure, and is stable up to 150°K, unless ionized by illumination or subthreshold-energy electrons. The free interstitial produced at the same time as the I-V_2 defect evidently can migrate at very low temperatures and produce an interstitial chemical impurity atom through a substitutional interaction. The primary thermal annealing stages are (a) recombination of close pairs near 65°K, (b) ionization and recombination of the (I-V_2)-type defect near 150°K, and (c) recombination of the remaining vacancy and chemical interstitial impurity near room temperature. Since the stability of both close pairs and nonreorientable divacancies depends on the respective charge state, the annealing temperature is markedly reduced by illumination or by ionizing radiation.

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