Mem. Fac. Lit. & Sci., Shimane Univ.,
Nat. Sci., 8, pp. 49–59, March 10, 1975

Annealing of *p*-Type Germanium Irradiated with Gamma Rays at 190K or at Room Temperature

Kazuyoshi ITO and Masahiro OKA

Department of Physics, Faculty of Literature and Science, Shimane University, Matsue, Shimane

(Received November 5, 1974)

Annealing of radiation induced defects in *p*-type germanium was studied by measuring minority carrier lifetime. The activation energy and the reaction order of the higher temperature stage (130°C–180°C) were dependent on the irradiation temperature. These values for indium-doped samples irradiated at room temperature were 1.04 eV and 2nd order, and those for the sample irradiated at 190 K were 1.33 eV and 1st order. The similar behaviour was also observed in gallium-doped samples. The higher temperature stage was larger and the lower temperature stage (20°C–60°C) was smaller for room temperature irradiation than irradiation at 190 K. A recombination center located at 0.06 eV above the valence band was removed through the intermediate temperature stage (80°C–125°C) and the higher temperature stage. The shallow trap, which was formed at 0.13 eV below the conduction band by the annealing to 60°C, disappeared in the intermediate temperature stage. Deep trap grew up simultaniously at the expense of the shallow trap and was not affected by further annealing to 200°C.

§ 1. Introduction

Investigation of the annealing behaviour of gallium- and indium-doped germanium was made by Saito et al.[1–3] In their stage V which occurs above 380 K, both the carrier concentration and the mobility restore their perirradiation values. The activation energy for the annealing was found to be 1.2 eV for gallium-doped samples and 1.6 eV for indium-doped ones. The annealing kinetics was roughly of second order for both impurities. The behaviours in the stage appears to correspond to those observed by Brown et al.[4]

The annealing stage which was similar to the stage V was also observed by Higashinakagawa et al.[5] They studied the annealing behaviours of *p*-type germanium after ^{60}Co gamma irradiation at 20°C. The annealing took place in an almost single stage centered at 390 K. From isothermal annealing study of gallium-doped samples, this stage was found to be represented by a second order process with an activation energy of 1.4 eV. Annealing curves of indium-doped samples were roughly fitted with a first order process and the activation energy was obtained to be 1.0 eV. They suggested that the annealing defects were some complex defects which included an impurity atom, *i.e.* perhaps an impurity-vacancy or impurity-divacancy complex.

The authors[6] reported that three annealing stages were observed in the tem-

perature range 20°C to 200°C. The lower temperature stage (LT stage) was observed in the temperature range 20–60°C. Isochronal annealing was dependent markedly on the impurity concentration. As the impurity concentration increased, the LT stage increased in importance. The activation energy and the frequency factor of the LT stage were dependent upon the covalent radii of the impurities. The activation energies were obtained to be 0.88 eV and 0.6 eV for indium-doped samples and gallium-doped ones, respectively. The reaction orders of the LT stage were unity. The order of reaction for the LT stage decreased with increasing indium concentration. By a similar treatment of the entropy factor to silicon, the number of sinks for the gallium-doped sample was calculated to be about $10^{15}/cm^3$, which was of the same order as the gallium concentration. The defect which migrates in the LT stage can be assumed to be a complex [impurity (sub.)·vacancy]. The defect makes an association with an impurity (sub.) resulting an association [impurity $(sub.)_2$·vacancy]. The higher temperature stage (HT stage) was observed in the temperature range from 130°C to 185°C and intermediate temperature stage (IT stage) was in the range from 80°C to 125°C. As the indium concentration increased, the HT stage was progressively eliminated. On the other hand, gallium doping appeared to suppress it. The activation energy of the HT stage was dependent on impurity species. The activation energies were obtained to be about 1.5 eV and 1.0 eV for gallium-doped samples and indium-doped ones, respectively. The order of reaction for the HT stage generally decreased with increasing impurity concentration. Considering these results and the discussions on the recombination behaviours, a tentative model for the IT stage and the HT stage was proposed. In the IT stage, the remaining [impurity (sub.)·vacancy] complex breaks up. The released vacancy may interact with the [$impurity_2$·vacancy] complex and form an [$impurity_2$·divacancy] complex, or it may be annihilated at an [impurity (int.)·impurity (sub.)] complex throughout the IT and the HT stages.

This work is concerned with the annealing of defects which migrate at the three stages. Minority carrier lifetime and trapping measurements have been used to study irradiation induced states. The experiments extend the results of the previous paper[6] to including the details of recombination and trapping effects, and to providing information about defects which may have annealed at these stages. It was also noted that the rate of production of a certain defect by Co 60 γ-rays in germanium was strongly dependent on the temperature at which the irradiation was made.

§ 2. Experimental Procedures

The samples were *p*-type germanium single crystals doped with gallium or indium. The impurity concentration was in the range between 1×10^{13} and 5×10^{15} cm^{-3}. The specimens were etched with CP–4 etching solution and sealed in a Pyrex tube. The irradiation was made at room temperature or at 190 K with γ-rays from a Co 60 source.

The nature of radiation-induced defects in *p*-type germanium was studied with

measurement of minority carrier lifetime. Measurements of lifetime carried out by detecting time decay in absorption of microwave power by a specimen inserted in a waveguide. No ohmic contact was necessary on the specimen and diffused-in impurities or dislocations which resulted from preparing contacts were avoidable. The measurement of temperature dependence of lifetime was made within the controlled temperature ramge from 80 K to 300 K and the reference temperature of the measurements was 20°C.

The samples were isochronally annealed for 20 min periods with 10°C steps between 20°C and 200°C. The parameters plotted in the annealing data are the unannealed fraction in minority carrier lifetime. The fraction not annealed, f, is calculated from the relation,

$$f=\frac{1/\tau_t-1/\tau_0}{1/\tau_{AB}-1/\tau_0}, \tag{1}$$

where τ_t is the minority carrier lifetime after annealing for time t, and τ_0 and τ_{AB} are the lifetime before and after irradiation, respectively. Other experimental details are included in previous papers[6,7].

§ 3. Experimental Results and Discussions

The isochronal annealing curves for the gallium-doped samples are shown in Fig. 1. The following sample designation is used; the first two letters denote the chemical symbol for the doping agent, the next number is resistivity in ohm-cm and the last is the series number of samples. The LT stage was strongly dependent on the irradiation temperature. For the case of the sample irradiated at 190 K, 25% of the induced

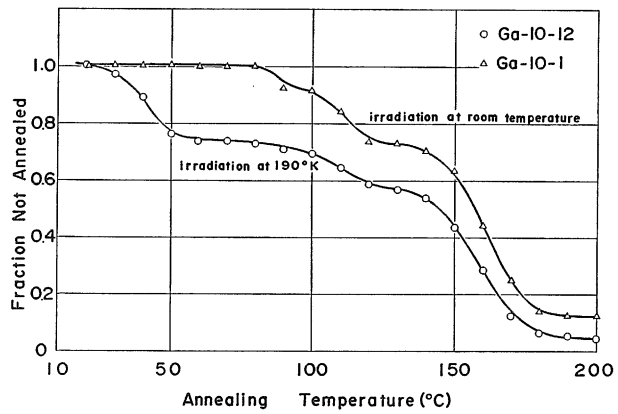

Fig. 1. Dependence of the annealing curves of gallium-doped samples on the irradiation temperatures.

change in lifetime was removed in the stage. In contrast, there was no anneal in the LT stage for the material irradiated at room temperature. It is suggested that the LT stage for Ga–10–1 occurs during irradiation at room temperature.

Fig. 2 shows the influence of irradiation temperature on the annealing behaviours of indium-doped samples. In–10–7 and In–2–2 were irradiated at room temperature

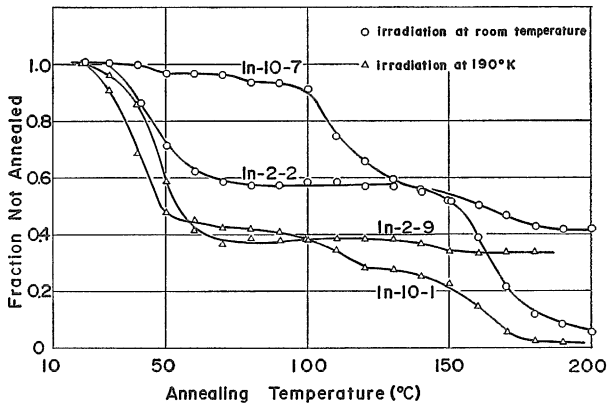

Fig. 2. Dependence of the annealing curves of indium-doped samples on the irradiation temperatures.

and others at 190 K. The amount of annealing in every stage was found to be dependent on irradiation temperature. The LT stage was prominent in the case of samples irradiated at 190 K, i.e., In–10–1 saturates with about 40% of the induced change remaining and the corresponding anneal in In–10–7 reaches a plateau after removing few per cent of the induced change in lifetime. It is suggested that the concentration of the defects associated with the LT stage is strongly dependent on the temperature where the bombardments are made. The HT stage of In–2–9 irradiated at 190 K was almost completely eliminated, but 17% of induced change was annealed in the HT stage for In–2–2 irradiated at room temperature. This result indicates that for the case of irradiation at 190 K a defect may go to sinks and is stored in the form of the stable complexes in the LT stage, but for In–2–2 a fraction of the same defect at the end of the LT stage is considerable. Accordingly, in the sample irradiated at room temperature, initial concentration of defect which moves in the HT stage is larger than that for 190 K irradiation.

G. K. Wertheim[8] proposed an explanation of the dependence of the defect production rate on irradiation temperature. The decreased defect density obsreved after low temperature irradiation was consider to be due to the production of a metastable vacancy-interstitial pair which might either anneal or form the defect. In a later paper,[9] investigation of the production of oxygen-defect complexes was reported. The exponential dependence of the production rates as a function of the irradiation

temperature, T, was expressed by the equation

$$\frac{d\alpha}{d\phi}=A\exp(-\Delta E/kT), \tag{2}$$

where ΔE is 0.01 eV, α is the optical absorption coeficient, ϕ is the incident electron fluence and A is a constant. This effect was also interpreted in terms of a metastable vacancy-interstitial pair model of defect production.

In view of the dependence of the production rates on irradiation temperature, concentration of [impurity (sub.)·vacancy] complexes after 190 K irradiation may be less than that after irradiation at room temperature, and a fraction of remaining complexes at the end of the LT stage in the sample irradiated at 190 K will be small. As shown in Table 1, these effects can be observed in the facts that the reaction orders

TABLE 1. SUMMARY OF ANNEALING DATA FOR THE HIGHER TEMPERATURE STAGE.

Sample	Act. energy (eV)	Freq. factor (sec^{-1})	Reaction order	Irradiation
In–36	1.03	3×10^{8}*	2nd	at room temp.
In–25	1.02	2×10^{8}*	$\lesssim$2nd	at room temp.
In–10	1.04	4×10^{8}*	2nd	at room temp.
In–10	1.33	9×10^{11}	1st	at 190 K
In–2		1×10^{8}**	1st	at room temp.
Ga–36	1.55	2×10^{14}*	2nd	at room temp.
Ga–10	1.42	1×10^{13}*	2nd	at room temp.
Ga–10	1.27	2×10^{11}	1st	at 190 K
Ga–1	1.57	4×10^{15}	1st	at 190 K

* These values were approximately obtained from the characteristic decay time.

** The frequency factor for In–2 was evaluated under the assumption that activation energy was about 1.0 eV. (from ref. 6)

of In–10 and Ga–10 shift from 2nd to 1st as the irradiation temperature is reduced. The result implies a decreasing concentration ratio, defects to sinks. On the other hand, the dependence of the activation energy of the HT stage on the irradiation temperature was observed in the materials doped with indium or gallium. The activation energy for the annealing was found to be 1.04 eV for In–10 irradiated at room temperature and 1.33 eV for the sample irradiated at 190 K, while 1.42 eV was obtained for Ga–10 irradiated at room temperature and 1.27 eV for that irradiated at 190 K. A singly activated rate process may be disturbed by the annealing defect themselves. The strains arising from the presence of defects in a crystal can alter the activation energy for the migration of the defect. If the activation energy has linear relation with the number of defects, the activation energy, E, will be expressed as

$$E=E_a-\beta C, \tag{3}$$

where E_a is the activation energy in the absence of all but one defect, C is the number of defect present and β is a proportionality constant. If the constant β has a positive value for an oversized impurity atom, the activation energy E for indium-doped sample decreases with increasing defect concentration. If Eq. (3) is valid, a negative value of β will be expected for the smaller sized gallium atom.

Temperature dependence of minority carrier lifetime for In–36–2 before and after irradiation and after successive annealings is shown in Fig. 3. Evidently a

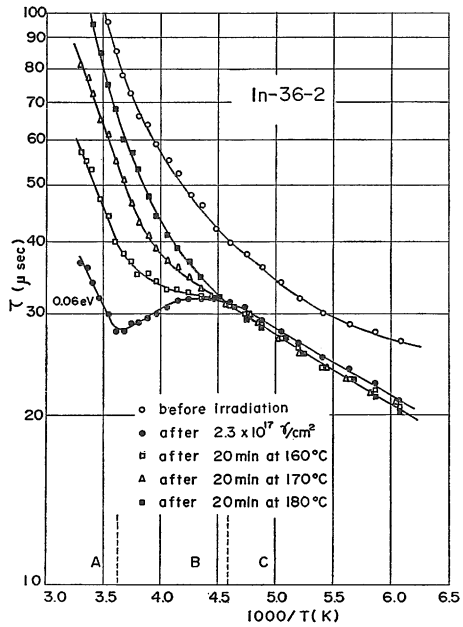

Fig. 3. The recombination behaviour of In–36 following irradiation by Co 60 gamma rays and successive annealings. A recombination level at $E_v+0.06$ eV is dominant immediately after irradiation.

recombination level located at 0.06 eV from the valence band was formed by irradiation. The effect of coupled levels, the recombination level and the trapping level, was observed in the region from 240 K to 280 K ($1{,}000/T=3.6\sim4.2$). As the annealing proceeded, the lifetime in region A, where recombination process was dominant, increased as the irradiation induced centers were removed. The recombination level at $E_v+0.06$ eV disappeared after isochronal annealing to 180°C. An effect of the trap observed in region B was easily removed by the annealing to 160°C. It is suggested that the trapping center is annealed out in the initial stage of the HT annealing. Another interesting feature of Fig. 3 is that the lifetime below 220 K was not affected by the isochronal annealing to 180°C. Further annealing of a sample from the same ingot show-

ed no further change in lifetime up to 250°C.

Similar features are observed in Fig. 4 for In–25–1. Both the recombination center and the trapping center were removed by the annealing. The decay time in the region C ($1{,}000/T > 3.8$) was kept almost constant against annealing. It is evident from Fig. 4 that the recombination level at $E_v + 0.06$ eV is removed in the HT stage and the coupled levels come to have no effect on the lifetime in the initial stage of the HT annealing.

Fig. 5 exhibits the temperature variation of lifetime for In–10–3 following ir-

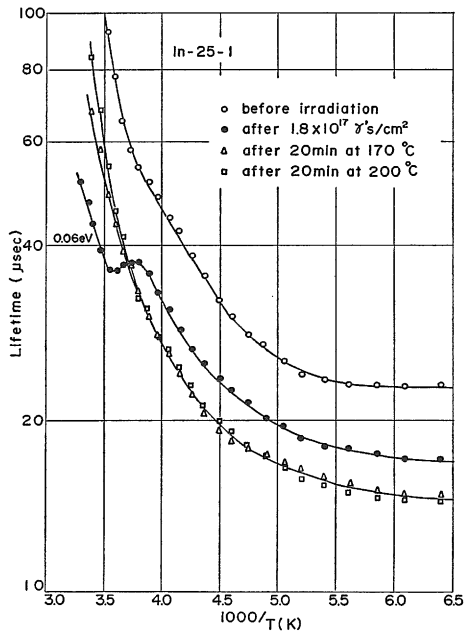

Fig. 4. The recombination behaviour of In–25 following irradiation by Co 60 gamma rays and successive annealings.

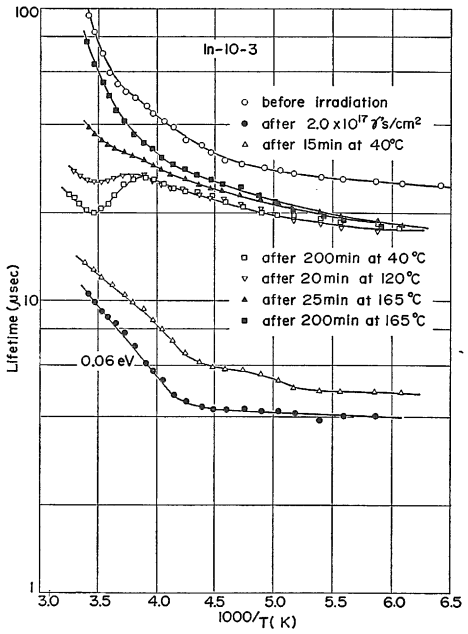

Fig. 5. The recombination behaviour of In–10 following irradiation by Co 60 gamma rays and successive annealings.

radiation at 190 K and successive annealings. The recombination center located at 0.06 eV above the valence band was dominant at high temperatures immediately after the irradiation of 2×10^{17} photons/cm^2. The lifetime in the temperature range above about 240 K (region A) increased with successive annealings in the LT stage. In addition, trapping was observed in the last stage of the LT annealing. After 200 min annealing at 40°C, temperature dependence of lifetime was similar to that of In–36 observed immediately after irradiation at room temperature (refer to Fig. 3). From this result it is suggested that the LT annealing of lightly doped sample proceeds during irradiation at room temperature. The annealing behaviour of lifetime for In–

10–3 was also similar to that of In–36 or In–25, in view of the temperature dependence. The disappearance of 0.06 eV level in the HT stage was observed in all indium- or gallium-doped samples. As shown in the curves obtained after annealing at 165°C, there is no indication of traps. It is suggested that the shallow trap is easily removed by the annealing in the IT stage. The lifetime in the region below 250 K ($1{,}000/T > 4.0$) was almost independent of annealing in the IT stage and the HT stage.

In order to discuss the creation of the shallow trap, plots of lifetime vs. reciprocal temperature after successive annealings in the LT stage are shown in Fig. 6. It was observed that the decay time in the trapping region increased until a new indication of trap became dominant at the end of the LT stage. In region A, the lifetime increased with successive annealings.

Fig. 7 shows the temperature dependence of lifetime for gallium-doped germanium

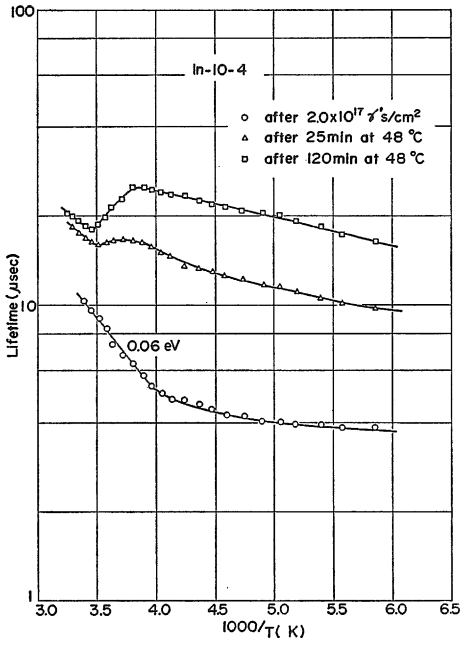

Fig. 6. The recombination behaviour of In–10 following irradiation by Co 60 gamma rays and succesive annealings in th LT stage.

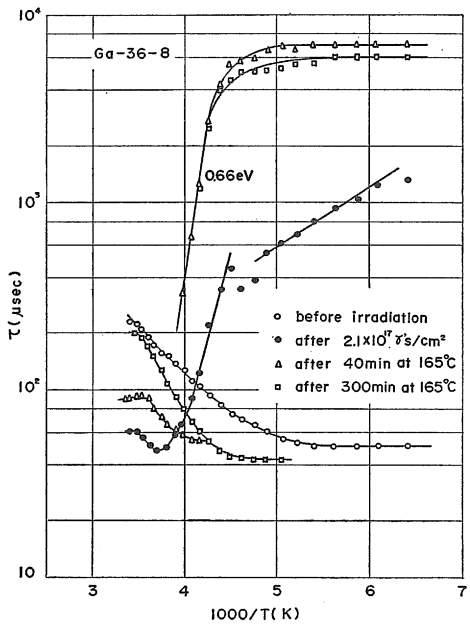

Fig. 7. The recombination behaviour of Ga–36 following irradiation by Co 60 gamma rays and successive annealings. A deep trap at $E_c - 0.66$ eV is dominant after annealing.

immediately after an irradiation of 2.1×10^{17} photons/cm^2 and subsequent annealings. The various recombination and trapping regions are evident in this figure. At lower temperature, a deep trap was observed and the decay curve showed a long tail. In region C, the slope of the curve became gentler under the influence of shallow traps.

As shown in previous papers[7,10], the shallow traps were dominant after irradiation of 2.6×10^{17} photons/cm^2. Therefore, in the temperature region B and C, the shallow traps obscure the slope of the curve to the extent that a fale indication of the trap position is obtained. As the annealing of the shallow traps proceeded, the decay time in region B increased. At the same time, the effect of the deep trap at $E_c-0.66$ eV became dominant. No further change in the decay time was observed after additional 300 min annealing at 165°C. This is suggests that the defect associated with the deep trap has a high thermal stability. The lifetime at above 0°C (region A) was almost restored to its pre-irradiation value after successive annealings.

The characteristics of the trapping center are obtained from region C ($1{,}000/T>5$) of Fig. 7. Since the decay time in the region is $(c_{pt}p_0)^{-1}$, where c_{pt} is the capture coefficient for holes at a trapping center and p_0 is the equilibrium concentration of holes, the cross section for holes of the deep trap can be determined from the curve in region C. The hole capture cross section was calculated to be 1.9×10^{-18} cm^2, by using the balue of p_0, 1×10^{13} cm^{-3}, and the decay time 6.5×10^{-3} sec at low temperatures. It is evident from the small value of the cross section that this trap is repulsive to holes.

Figs. 8 and 9 show the recombination behaviour of Ga–10 following irradiation

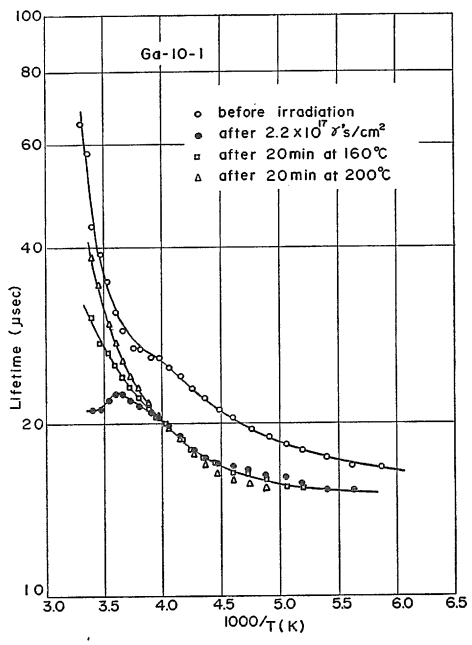

Fig. 8. The recombination behaviour of Ga–10 following irradiation by Co 60 gamma rays and successive annealings.

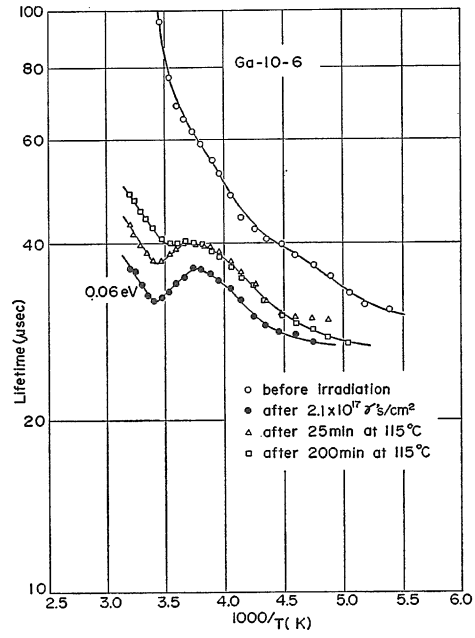

Fig. 9. The recombination behaviour of Ga–10 following irradiation by Co 60 gamma rays and successive annealings in the IT stage.

and successive annealings. The features observed in these figures are similar to that of Fig. 3. In Fig. 8, the influence of the coupled levels is observed even at room temperature immediately after irradiation. But the effect of the trap was easily removed by the annealing at 160°C. The temperature dependence of the lifetime was measured to investigate the formation and the disappearance of levels in the IT annealing stage (Fig. 9). A shallow trapping center was found to be formed by the irradiation and the effect of recombination center located at 0.06 eV above the valence band was dominant at high temperature. As the annealing proceeded, the decay time in region B increased, whereas the density of recombination center at $E_v+0.06$ eV became smaller but was not annealed out in the IT stage.

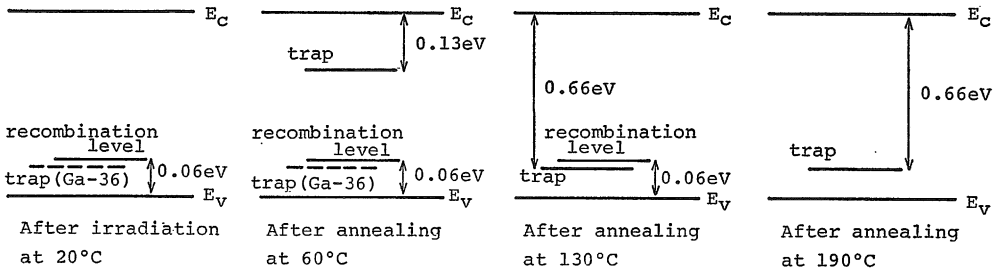

Fig. 10. Energy level scheme in irradiated p-type germanium.

The energy level scheme obtained in this investigation is summarized in Fig. 10. A recombination center located at 0.06 eV above the valence band was dominant after irradiation of $\sim 2.0\times10^{17}$ photons/cm^2 at room temperature or 190 K. A deep trapping level at 0.66 eV below the conduction band was observed in the sample containing little gallium. A new trap was formed at 0.13 eV below the conduction band by the annealing to 60°C. The shallow trapping level disappeared in the IT stage. After isochronal annealing to 190°C, the recombination level at $E_v+0.06$ eV was removed. However, the deep trap was not annealed throughout the course of the three annealing stages for the sample containing 1×10^{13} gallium atoms/cm^3.

As discussed in the previous paper,[6] the defect [impurity (sub.)·vacancy] migrates in the LT stage and makes a stable association [impurity (sub.)$_2$·vacancy]. A fraction of remaining [impurity (sub.)·vacancy] pair recovers presumably in the HT stage for high purity samples. As the annealing temperature is raised into the range of the IT stage and the HT stage, the association [impurity (sub.)·vacancy] begins to break up, releasing a vacancy back to the lattice. The vacancy may go to the [impurity$_2$·vacancy] complex and produce a [impurity$_2$·divacancy] complex, or it may go to an association [impurity (sub.)·impurity (int.)] and be annihilated.

The authors would like to thank Professor H. Saito, Professor M. Hirata, Dr. N. Fukuoka and Mr. Y. Tatsumi of Osaka University for their useful discussions.

References

1) H. SAITO, N. FUKUOKA and Y. TATSUMI: Radiation Effects **8** (1971) 171.
2) H. SAITO, N. FUKUOKA, H. HATTORI and J. H. CRAWFORD, Jr.: *Radiation Effects in semiconductors* ed. F. L. Vook (Plenum Press, NewYork, 1968) p. 232.
3) H. SAITO, N. FUKUOKA, H. HATTORI and J. H. CRAWFORD, Jr.: *Lattice Defects in Semiconductors* ed. R. R. Hasiguti (Univ. of Tokyo Press, Tokyo, 1968) p. 199.
4) W. L. BROWN, W. M. AUGUSTYNIAK and T. R. WAITE: J. appl. Phys. **30** (1959) 1258.
5) I. HIGASHINAKAGAWA, S. ISHINO, F. NAKAZAWA and R. R. HASIGUTI: *Lattice Defects in Semiconductors* ed. R. R. HASIGUTI (Univ. of Tokyo Press, Tokyo, 1968) p. 211.
6) K. ITO, M. OKA and H. SAITO: Japan. J. appl. Phys. **12** (1973) 1475.
7) K. ITO, M. OKA and H. SAITO: Mem. Fac. Lit. & Sci., Shimane Univ., Nat. Sci. **5** (1972) 29.
8) G. K. WERTHEIM: Phys. Rev. **115** (1959) 568.
9) R. E. WHAN: *Radiation Effects in Semiconductors* ed. F. L. Vook (Plenum Press, NewYork, 1968) p. 195.
10) K. ITO, M. OKA and H. SAITO: J. Phys. Soc. Japan **31** (1971) 305.