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Effects of Gamma Irradiation on Minority Carrier Lifetime in p-Type Germanium

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Mesurements of carrier lifetime from 150 to 300°K have been made on samples of indium- and gallium-doped germanium after gamma irradiation at room temperature. In gallium-doped crystals, the formation of traps was observed only in a low resistivity material. The positions of the trapping levels were found to be 0.66 eV and 0.13 eV from the conduction band. It seems that the deep trap exhibits multiple trapping. The shallow trap was annealed readily at the stage around 430°K but the deep trap was stable by annealing at this temperature. No trapping level was introduced by the irradiation into indium-doped sample.

§ 1. Introduction

Lifetime of minority carriers in germanium depends on a structure-sensitive property of the material. The recombination prcess takes place through the medium of defects of some sort in the crystal. Therefore, minority carrier lifetime is a good measure of defects and has been used in many studies on radiation damage in semiconductors. The reports on study of the more complicated behavior of p-type germanium have been published less than n-type material. One of the reason is possibly that the rate of change in Hall coefficient as well as lifetime with radiation fluence is much smaller for p-type germanium than for n-type.[1-3]

Recently the studies of radiation effects on p-type germanium are earnestly proceeded again by some workers[4-13]. Brown et. al[1]. reported the annealing results of defects in p-type germanium after 1.0 MeV electron irradiation at 79°K. They showed that at about 200°K a rearrangement of a defect center occurred, exhibiting first order kinetics, but with a time constant which was strongly dependent upon the charge state of the defect. At higher temperature, about 400°K, there is annealing process which removes almost all the irradiation-induced donors. The recovery process is nearly second order and the activation energy is remarkably large, approximately 2.1 eV.

On the simplest condition where the temperature was maintained at the lowest value

in order to restrict thermal motion of the defects, E. E. Klontz et al.[9,10] studied the radiation effects in non-degenerate p-type germanium. Lattice defects are produced by 1.0 MeV electrons at 10°K. No change of electrical properties is observed immediately after electron irradiation. The defects can be revealed by illumination with light passed through a germanium filter, having energy less than the band gap. During illumination, the hole concentration decreases with time in two exponentials whose time constant are about 6 hr and 40 hr. Subsequent isochronal annealing produces a continuous recovery of hole concentration in the range 40～80°K. If the ionization of the defects by the filtered light is not complete, a transformation of the defects occurs in temperature range from 100 to 150°K. They called the defect configuration "the two state defect". The two-state defects break up near 200°K, leaving a number of donors behind it. At about 400°K, there is final annealing stage which eliminates these donors. Both 200°K and 400°K annealing stages are similar to the stages observed by Brown et al[1].

The investigations of the annealing behavior of gallium-and indium-doped germanium have been made by Saito et al.[5-7] The irradiation is made with 1.5 MeV electrons at 77°K. Five annealing stages for gallium-doped crystal and four annealing stages for indium-doped one are observed in the temperature range 80～400°K. The stage I is observed in a temperature range 80～140°K. They suggested that the defect which moved in the stage was $Vac.^{+}$ and made association with $Imp.(Sub.)^{-}$ resulting in an association $[Vac.\cdot Imp.(Sub.)]^{+}$. The activation energy is found to be 0.1 eV, regarded to be that of the migration of vacancies. The stage III which is observed in the range 220～270°K is strongly dependent on the type and concentration of the impurity. In this stage all of the radiaton induced traps are destroyed. Considering from the experimental evidences, they conclude that the defect which anneals in the stage is an interstitial impurity atom with double plus charge acting as a trapping center. In the stage V which occurred above 380°K, both carrier concentration and mobility was restored to their preirradiation values. The activation energy was found to be 1.2 eV for gallium-doped samples and 1.6 eV for indium-doped ones.

Curtis et al.[14-17] studied the effects of irradiation on the lifetime of p-type germanium. The informations obtained by measurements of lifetime are few and no experiments have been made thereafter. The temperature dependence of lifetime for p-type germanium measured after gamma irradiation shows the formation of recombination level of 0.05 eV.[14] For fission-neutron-irradiated samples the recombination level position is about 0.09 eV.[14] The small temperature dependence observed might be due to a variation in electron capture probability.[16] The observed behavior can not be explained on the basis of a simple one-levpel recombination center, but must be based on a two-level recombination center.[14, 15]

The amount of published works on p-type germanium, especially measurements of carrier lifetime, is small compared to that on n-type material. In the present work, minority carrier lifetime and trapping measnrements are used to investigate the irradiation induced defects. Generally, recombination and trapping levels tend to be located deep in the band gap, which are difficult to observe with Hall effect or resistivity measurements. It is often possible to detect the influence of recombination center densities well below the carrier concentrations so that a relatively small change in structural damage may be studied effectively. The technique employed in this study is

measurement of the photoconductive decay time over a range of temperatures. The irradiation of both indium- and gallium-doped specimens with a wide range of hole concentration was carried out at room temperature and measurements of lifetime were made after successive exposures.

The purpose of this paper is to present the interpretation of the lifetime date in terms of the properties of defects induced by irradiation. Discussion of the annealing behavior, which arise necessarily in the studies of radiation-induced defects, will be reserved for a later paper.

§ 2. Experimental Procedure

This study was made on samples doped with gallium or indium atoms. The impurity concentration is in the range between 1×10^{13} and 1×10^{15} cm^{-3}. In order to minimize surface effects, large samples were cut to dimensions of $2.8\times2.8\times16$ to 22 mm^3 by diamond wheel. D. Navon et al.[18, 19] reported that the etched-surface lifetime does not vary with the dimensions of the sample until parhape its smallest dimension is 0.5 mm or less. The surfaces were prepared by etching with CP-4 and washing with distilled water by supersonic washer. When the samples are left in air, lifetime decreases with time due to the change in the surface recombination velocity. For the purpose of minimizing this effect, the sample was sealed in a Pyrex tube evacuated to about 1×10^{-2} Torr after replacing the air inside the tube with nitrogen gas.

The gamma irradiation were carried out at room temperature with a Co 60 source of approximately 50 curies, providing about 3×10^5 röntgen per hour at the sample.

Measurements of lifetime were made by measuring the the photodecay in absorption of microwave power. Generally in the photoconductive method, contacts must be used on the ends of the sample. However, it is difficult to make good ohmic connections for semiconductors. Thereupon the electrodeless technique was proposed by Ramsa et al.[20] in the use of microwave absorption. Changes in the absorption constant, α, can be approximated as linear relation with changes in the power absorbed by the semiconductor. For germanium with the order of conductivity, $\sigma \ll \omega\varepsilon$, the absorption coefficient is given by

$$\alpha = 1635\ \sigma/n \quad \text{dB/m}$$

where ε is the dielectric constant and n the index of refraction. Thus, the changes in

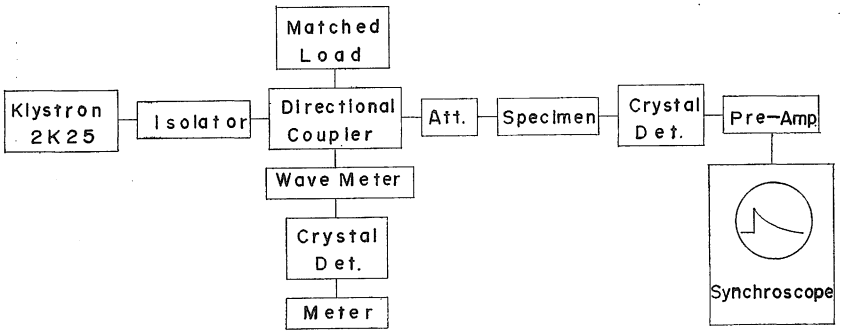

Fig. 1 The block diagram of lifetime measurements.

microwave power with time will vary linearly with the changes in conductivity of the sample, therefore the minority carrier lifetime must be equal to the time constant of the decrease in absorbed power.

Fig. 1 indicates schmatically the experimental arrangement used in measurements of lifetime. A well regulated klystron source provided 10 Gc microwave. The microwave passed through the specimen and absorbed power measured with a crystal detector followed by a synchroscope. Xenon flash tube was used as the light source injecting excess carriers. The illuminating system can deliver pulse of light with a very short turn-off time, 0.5 μ sec. This is sufficiently short compared with the lifetime of specimens. The concentration of excess carriers was maintained at a level such that the sample conductance changed by less than 5 per cent in order to minimize errors due to the dependence of lifetime upon injection level. Under this condition the decay curve was comfirmed to be exponential. The reference temperature of all measurements was 293°K. In the case of measuring temperature dependence of lifetime, the measurement was made within the controlled temperature range of about 80°K through 300°K by the blowing of cold nitrogen gas. A copper-constantan thermocouple was used for the measurement of temperature.

§ 3. Results and Discussions

Here, the basic aspects of the recombination of minority carriers in p-type germanium are treated first of all. It will help, since the behaviors of p-type germanium are complicated although the alternation of the analysis of n-type material for p-type can be easily made by exchanging the roles of electrons and holes. In the previous section the decrease of lifetime of p-type material left in air is descrived. Fig. 2 is a plot of normalized lifetime, τ/τ_0, vs the period of duration that the samples are left in air or

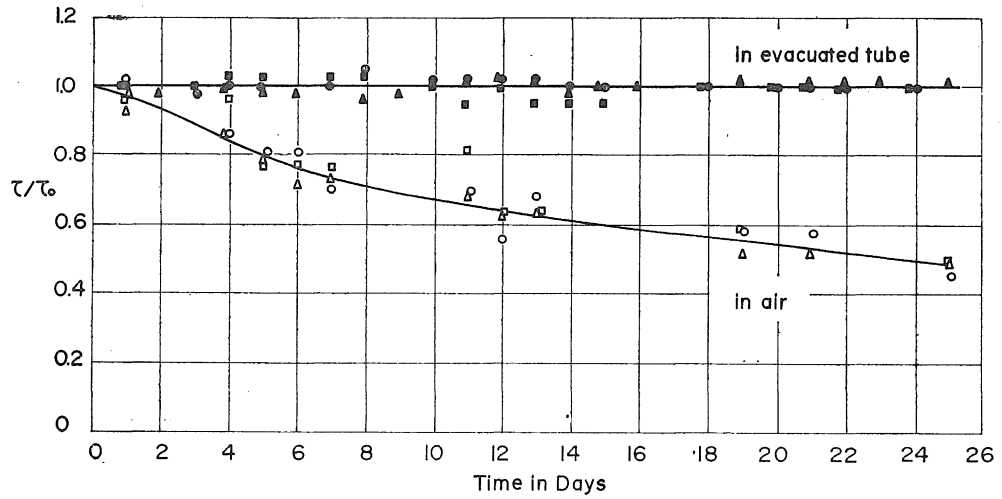

Fig. 2 The influence of air on the surface of germanium crystals.

in the evacuated tube, where τ_0 is the lifetime immediately after etching. The lifetime of sample left in air was not stable but decreased with time, while that for the other

ones in the evacuated tube were constant with respect to time. This result indicates the effects of surface recombination on the measured lifetime due to oxidation of sample surface. Although the preparation of samples including evacuation to 10^{-2} Torr is good to keep the lifetime stable at room temperature, but there is a possibility that some surface recombination center is introduced in the follwing heating experiment at higher temperatures. To examine the effect of heat treatment on the unirradiated specimens, the 20 min isochronal heating in the temperature range from 20°C to 400°C was made at 10°C interval. The result is shown in Fig. 3. In-36-5 was sealed in Pyrex tube

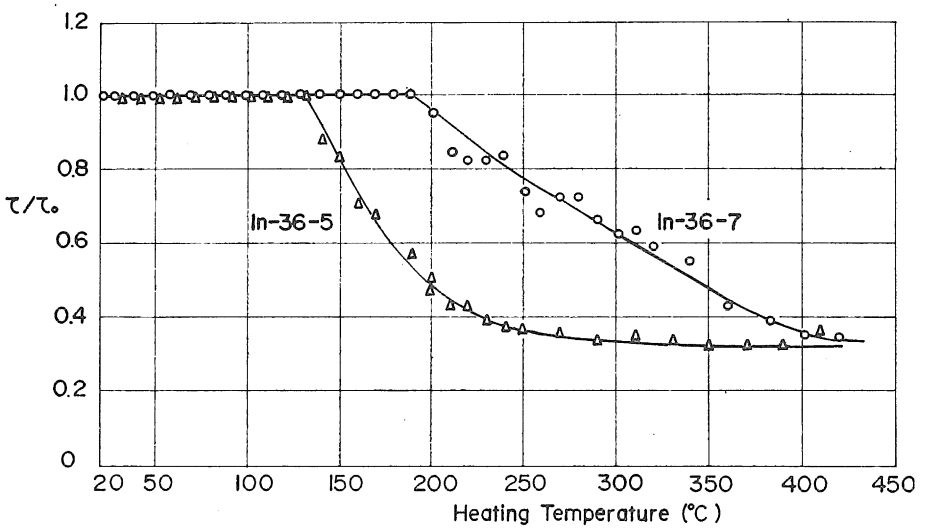

Fig. 3 The effect of heat treatment on the unirradiated samples.

merely evacuated to about 1×10^{-2} Torr and In-36-7 was evacuated to the same value after replacing the air inside the tube with nitrogen gas. Such conclusions can be drawn immediately from this figure that lifetime depends markedly on ambient atmosphere, especially oxygen, and the technique adopted for control of the surface effect is adequate up to 200°C where the annealing at the highest temperature is carried out.

The effects of gamma irradiation on minority carrier lifetime in p-type germanium was investigated in two different ways. One is the measurement of the change in lifetime with increasing radiation dose and the other is that of the temperature dependence of lifetime after successive irrdiations.

The relation between lifetime, τ, and the density of recombination centers, N_r, is given by[21]

$$\frac{1}{\tau}=\frac{1}{\tau_0}+N_r\sigma_c v f_B(E_r-E_F) \tag{1}$$

and $\Delta\frac{1}{\tau}=\frac{1}{\tau}-\frac{1}{\tau_0}$, $N_r=\Delta(E_B)\phi$,

where τ_0 : minority carrier lifetime before irradiation,

σ_c : cross section for minority carrier capture,
v : thermal velocity of carriers,
$f_B(E_r-E_F)$: a function of the location of the recombination centers, E_r, with respect to the Fermi level, E_F,
$\Delta(E_B)$: cross section for the formation of recombination centers,
ϕ : integrated flux.

In addition, on the basis of the Hall[23]-Shochley-Read[24] recombination model, the recombination equation can be written for p-type germanium in which the Fermi level lies above the recombination level,

$$\tau = \frac{p_1}{c_n N_r p_0} \tag{2}$$

and $p_1 = N_v \exp[(E_v - E_i)/kT]$,

where c_n : electron capture coefficient,
p_0 : thermal equilibrium value of hole density,
N_v : effective density of levels for valence band,
E_v : energy of highest valence band level.

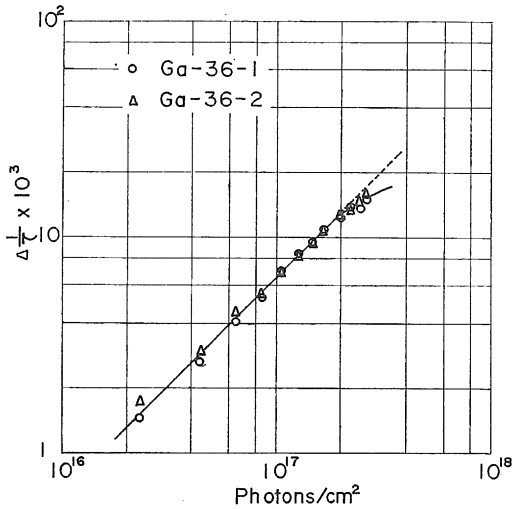

Fig. 4 $\Delta(1/\tau)$ of gallium-doped samples as a function of cumulative dose.

Fig. 4 illustrates the effect of successive irradiations on lifetime at room temperature where recombination process is dominant. $\Delta(1/\tau)$ is propotional to the cumulative dose until about 2×10^{17} photons/cm^2. In agreement with Eq. (1), this result indicates a linear relation between N_r and ϕ. According to Eq. (2), when ϕ is high enough to affect the carrier concentration, p_0, the effect of increasing radiation induced recombination centers on lifetime is partly masked by the change in p_0. However, this was not observed until ϕ reached 2.3×10^{17} photons/cm^2 for indium-doped material and 2.6×10^{17} photons/cm^2 for gallium-doped material (see Fig. 5 and Fig. 6). Therefore, the total flux should necessarily be less than about 3×10^{17} photons/cm^2, in order to insure the analysis based on the recombination equations. For the case of n-type materials which contain antimony

atoms of the order of 10^{14} cm^{-3}, the limit is reported to be 3×10^{16} photons/cm^2. [22] The value for the p-type materials reported here is about ten times as large as that for the n-type.

Measurement of temperature variations of lifetime is one of the best tools for studying the recombination process. Fig. 5 is a plot of the logarithm of lifetime vs reciprocal

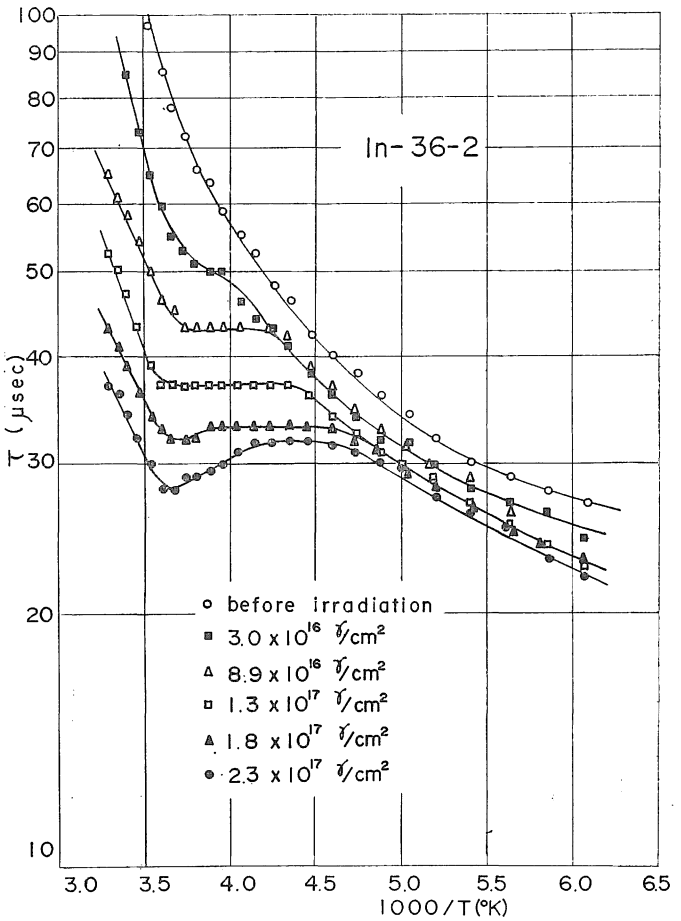

Fig. 5 The effects of successive irradiations on indium doped sample.

temperature after successive irradiations for sample In-36-2 which contains indium atoms of 3×10^{13} cm^{-3}. Above about 0°C ($1000/T > 3.66$) the lifetime decreased after successive irradiations owing to the increase in the concentration of radiation induced recombination centers, N_r. The result is in good agreement with the relation which is given by Eq. (2) in this temperature region. The position of the recombination level, $E_v+0.09$ eV, is obtained tentatively from the slope of ln τ vs $1/T$ in Fig. 5. However, in order to obtain the energy-level position more precisely it is necessary to consider the dependence of electron capture cross section. Then the recombination level located 0.06 eV from valence band is determined from analysis of the slope of τ vs $1/T$ curve. Curtis[14] observed the formation of recombination level of 0.05 eV for p-type

samples (12 and 2.5 ohm-cm) after exposures of 8.8×10^{16} and 1.4×10^{17} photons/cm^2, respectively. This level may be refered to the $E_V+0.06$ eV level observed in present work. They proposed that the results for p-type germanium included either a strong dependence of capture probability on temperature or recombination at a shallow level[16] and that behavior might be explained on the basis of coupled levels involving recombination in the presence of traps.[15] In Fig. 5, the plot of recombination lifetime shows a strangely behaving curve in the region from 130°K to 270°K ($1000/T = 3.7\sim4.5$). In this region the minority carrier lifetime is approximately temperature independent and this tendency is emphasized with successive irradiations. The fact may be interpreted to have been influenced by coupled levels, a recombination level and a trapping level. If this is the case, the position of the energy level can not be determined from the data in the temperature range.

The effect of successive irradiations on gallium-doped sample is shown in Fig. 6.

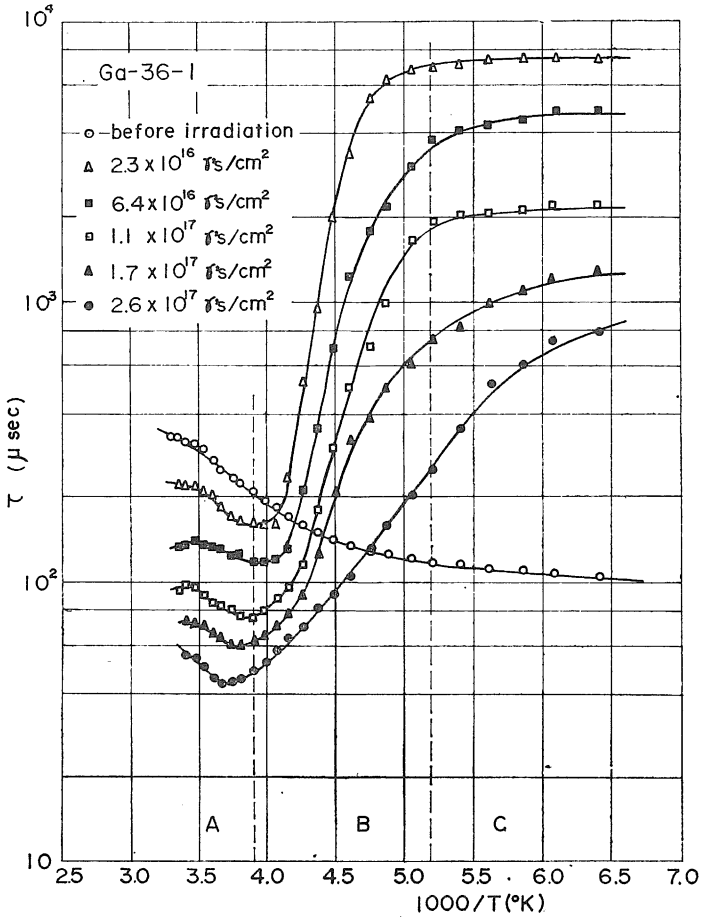

Fig. 6 The effects of successive irradiations on gallium-doped sample.

The carrier concentration of this sample is 1×10^{13} cm^{-3}. It is evident that a trapping level is formed after irradiation of these gallium-doped sample.[25] But, the formation of trap is not observed for indium-doped sample, as shown in Fig. 5, and the sample

doped with more gallium atoms (more than 10^{14} cm^{-3}).

Wertheim[26] treated the calculation of recombination in the presence of trapping level and this treatment was extended by Curtis et al.[15] and Streetman.[22] From higher temperature region A in Fig. 6, the characteristics of the recombination center is obtained and lifetime is dominated by Eq. (2). The position of recombination level is obtained from the slope of ln τ vs $1/T$. At lower temperatures, or in the region B, a trap is observed. For the case of this p-type material the proper expression of τ under the existence of trapping centers is

$$\tau = \frac{1}{c_{nt} n_{1t}} + \frac{N_t}{N_r n_{1t}} \left(\frac{1}{c_{nr}} + \frac{n_{1r}}{c_{pr} p_{1r}} \right) \tag{3}$$

where N_r : number of recombination centers,

N_t : number of trapping centers,

c_{nr} : electron capture probability at a recombination center,

c_{pr} : hole capture probability at a recombination center,

c_{nt} : electron capture probability at a trapping center,

n_{1t} : the electron concentration for the case in which the Fermi level lies at the trapping level,

n_{1r} : the electron concentration for the case in which the Fermi level lies at the recombination level,

p_{1r} : the hole concentration for the case in which the Fermi level lies at the recombination level.

If N_t is small compared to N_r in Eq. (3), the second term is negligible and then this equation can be written as $\tau = 1/c_{nt} n_{1t}$. This equation predicts that lifetime is not dependent upon the trap density in region B.

The decay time in Haynes-Hornbeck[27,28] treatment for trapping is given by

$$\tau = \tau_r + \tau_g + \tau_g \frac{\tau_r^0}{\tau_t} \tag{4}$$

where τ_g : mean time that the carrier spends in the trapping center before thermal re-excitation,

τ_r : recombination time,

τ_t : mean time that a electron spends in the conduction band before being trapped,

τ_r^0 : mean time that a electron spends in the conduction band before being captured by the recombination center.

In the Eq. (4), if the density of trapping centers is large compared to the density of recombination centers, the third term is dominant, since τ_t is very small. This decay is dominated by the multiple trapping process. For such a case, electrons are trapped very quickly by the attractive centers and after re-emission to the conduction band they are likely to be trapped again before being captured by the recombination centers. Here the change in conductivity is characterized by a decay with the long tail.

In the case of Fig. 6, at higher temperatures (region A) lifetime decreased after irradiation caused by radiation induced recombination centers. The position of the recombination center is at the same value of 0.06 eV above valence band as indium-

doped materials. Similar recombination level observed also for the sample doped with more gallium atoms. However at high temperatures ($1000/T > 3.5$) lifetime decreases with increasing temperature. This fact is accounted for the contribution to recombination of intrinsic carriers. From this temperature region, it is impossible to obtain the position of the recombination level with any accuracy. At lower temperatures(region B) the position of deep traps was found to be 0.66 eV below the conduction band, equivalent to $E_v+0.06$ eV, for the sample irradiated to a total flux of 2.3×10^{16} photons/cm^2. Since the trap lies nearly at the same position as the recombination level, it seems that the center effective for recombination in low resistivity material may be the same one which acts as a trap for higher resistivity material, and that the recombination levels at higher temperatures become the trapping levels at lower temperatures. Srour and Curtis[29] described that recombination at the trapping center became possible because of the large majority carrier concentration present in lower resistivity sample. In addition, Shulman[30] showed that the level which acts as a recombination center at room temperature became a minority carrier trap at lower temperatures. Curtis and Crawford[15] suggested that the trapping center might be present in gallium-doped specimens and might result from a gallium-defect complex. In his paper, the behavior observed in indium-doped material is somewhat different from gallium-doped one and there is no evidence for the trapping centers present. For the case of n-type materials, high purity antimony-doped material displays the presence of a trapping level, which is not effective in medium or low resistivity material.[15]

When the sample was exposed to gamma rays further, time of thermal release from the traps is decreased and the slope of the curve in Fig. 6 changes. On the base of Eq. (3), if the density of trapping centers, N_t, is less than that of recombination centers, N_r, the photodecay time should be independent of N_t in the temperature region B, where the thermal release from the traps is dominant. However, in the case of Fig. 6, the decay time becomes shorter with the increase N_t. Therefore, it seems that the density of the radiation induced trapping centers is larger than that of the recombination centers. From this fact and another one that the decay curve has a very long tail, it is suggested that the multiple trapping is occurring. If this is the case, the electron capture cross section of deep trap is considered to be very large, approximately the order of 10^{-13} cm^2 judging from the data of p-type Si.[27,28] After irradiation of 1.7×10^{17} photons/cm^2, the slope of the curve becomes gentler under the influence of shallow traps formed. After final irradiation of 2.6×10^{17} photons/cm^2, the shallow traps are dominant and its level position was found to be $E_c-0.13$ eV. The existence of the two trapping levels was also comfirmed from annealing experiment. The 20 minutes isochronal anneals in the temperature range from 290 to 470°K were made for both indium- and gallium-doped samples. It was found that there was a main recovery stage at about 430°K. After anneal at this temperature the density of recombination centers decreased and the recombination level at $E_v+0.06$ eV was almost removed. The shallow traps were apparently removed in this annealing stage but some fraction of the deep traps were still remained.

In conclusion $\Delta(1/\tau)$ is proportional to the cumulative dose up to about 2×10^{17} photons/cm^2. The behaviour of gallium-doped samples irradiated with gamma rays is characterized to form both the shallow trap ($E_c-0.13$ eV) and deep trap ($E_c-0.66$ eV).

The former is annealed readily at the stage around 430°K, but the latter behaving itself like multiple trapping center is stable by annealing at this temperature.

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