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ANNEALING OF THERMAL DEFECTS IN p-TYPE GERMANIUM

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Abstract: The thermal defects in quenched p-type Ge by isochronal and isothermal annealing were studied. Only one annealing stage in the temperature range from 650 to 700 K was discovered. This indicates the high stability of thermal defects. The annealing rate constant which does not depend on the dislocation density at the higher dislocation densities is given by $5.5 \cdot 10^{13} \exp(-2.30\ \text{eV/kT})\ \text{s}^{-1}$. The annealing process is well represented by first order kinetics. In the interpretation of experimental results the thermal defects were taken to be divacancies. Thus, the activation energy of $(2.30 \pm \pm 0.10)$ eV was explained as the dissociation energy of divacancy. If the migration energy of single-vacancy of 0.2 eV is correct, then the binding energy of divacancy in p-type Ge is (2.10 ± 0.10) eV.

1. Introduction

The lattice defects in Ge induced by quenching were extensively studied by their acceptor action[1].

It was experimentally confirmed[2-9] that the concentration of thermal acceptor v. s. quenching temperature above 1000 K follows the well-known Arrhenius relation. The formation energy of about 2 eV was obtained. This energy has generally been assumed to be the formation energy of single-vacancies in Ge. This assumption was supported by three facts:

— according to the James and Lark-Horovitz model[10] single vacancies in Ge should be acceptors with two energy levels,

— the theoretical calculations[11, 12, 13] predicted for the formation energy of single-vacancies in Ge the values from 1.90 to 2.65 eV, and

— the self-diffusion coefficient of Ge applying the radioactive isotope ^{71}Ge [14,15,16] was determined, whereby an activation energy of about 3 eV was obtained.

The activation energy of self-diffusion for a monovacancy mechanism is given by $Q^{SD} = E_{1V}^{F} + E_{1V}^{M}$, where E_{1V}^{F} and E_{1V}^{M} are the formation and the migration energies of single-vacancy, respectively. According to this relation the migration energy of single-vacancy in Ge should be about 1 eV. This value is close to the experimentally determined values of 1.2 eV[6] and 1.3 eV[17]. However, such values are incompatible with the value of 0.2 eV later found to be the migration energy of single-vacancy in Ge[18].

According to the high mobility of single vacancies in Ge[18, 19, 20] it is nearly certain that the relatively stable thermal acceptors are not single vacancies. They can be considered as the associations of single-vacancies themselves (divacancies or larger vacancy-clusters) or the associations with impurities and other lattice imperfections.

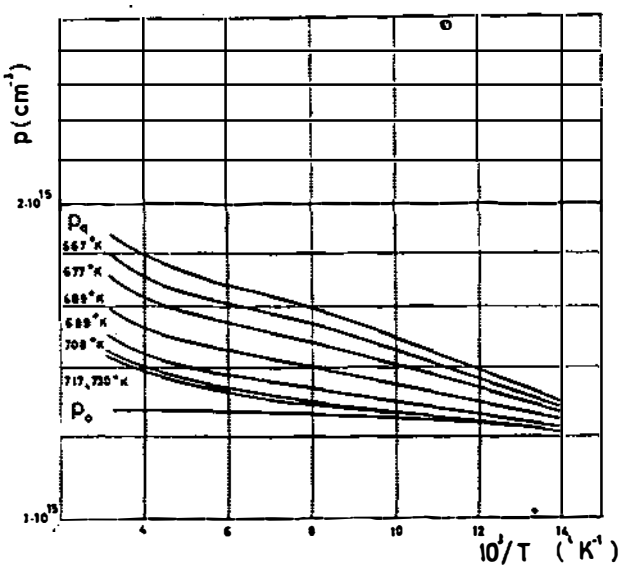

Fig. 1. Temperature dependence of hole concentration before quenching-p_o, after quenching-p_q and after successive isochronal anneals.

In the previous paper[21] the authors investigated the temperature and time dependence of thermal acceptor concentration in p-type Ge.

In the present paper the isochronal and isothermal annealing of thermal acceptors in quenched p-type Ge were studied. The main purpose of this work was to get some informations about the nature of thermal defects through the processes of their formation and annealing.

2. *Experimental procedure*

Thermal acceptors by original technique and experimental procedure[22] were studied. The samples were heated in high vacuum (10^{-7} mmHg) by resistance heating and cooled down to the liquid nitrogen temperature with an initial cooling rate of about 1000 K/s.

The rectangular samples ($20 \cdot 2 \cdot 1$ mm^3) of p-type Ge single-crystals with gallium concentrations $1.4 \cdot 10^{14}$ and $1.4 \cdot 10^{15}$ cm^{-3} were used. The nominal dislocation density of the samples was 300 cm^{-2}.

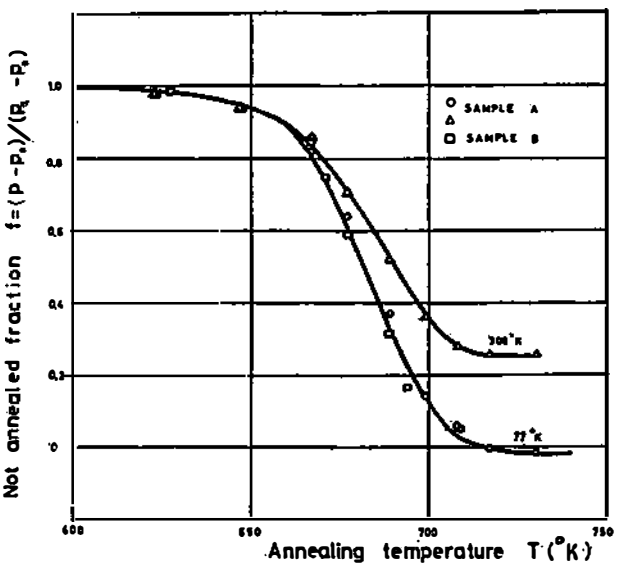

Fig. 2. Isochronal annealing of carrier concentration. The annealing time was 10 minutes at each temperature. The carrier concentration was measured at 77 K (○-sample A and □-sample B) and at 300 K (△-sample A).

The samples were prepared by standard technique (mechanical polishing, cleaning and etching in CP4-A solution). The electrical conductivity and the Hall coefficient in the temperature range from 77 K to 300 K before quenching, after quenching and after each cycle of the annealing were measured.

The Hall coefficient was measured with the magnetic field of 3600 Gauss. The concentration of carriers after quenching was calculated with a correction due to the magnetic field dependence of the Hall coefficient[14]. This correction was done comparing the Hall coefficients before and after the quenching. Such a comparison is possible since the gallium atoms are completely ionized at liquid nitrogen temperature. At this temperature the approximation of infinite magnetic field is correct even with the field of 3600 Gauss[25]. At higher temperatures the Hall coefficient must be corrected. For example, the correction factor at 200 K is about 25%.

3. *Results*

The hole concentrations before quenching, p_0, after quenching, p_q, and after each isochronal annealing, p, are shown in Fig. 1. The annealing time was 10 minutes at each annealing temperature. These results indicated two acceptor levels. The level with lower ionization energy disappears during the annealing.

The results of isochronal annealing are shown in Fig. 2 where the fraction not annealed, $f = (p - p_0)/(p_q - p_0)$, is plotted v. s. the annealing temperature. Two reference temperatures, 77 K (samples A and B) and 300 K (sample A) were used.

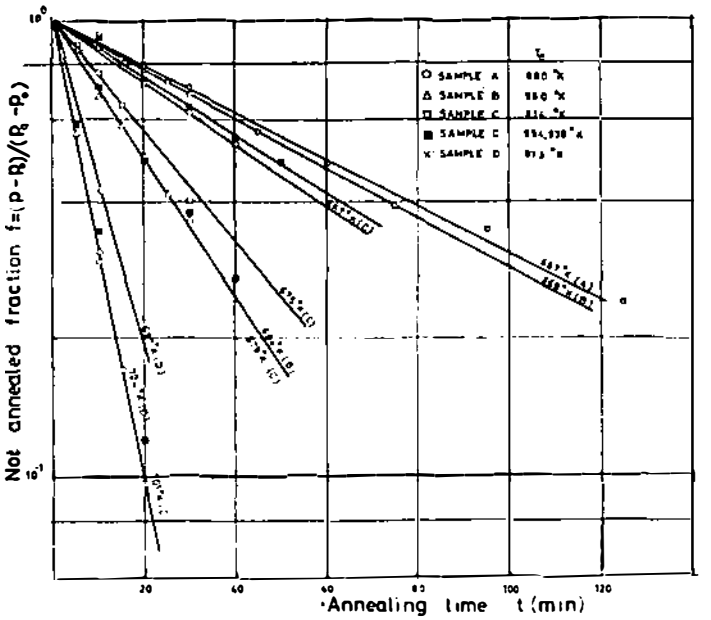

Fig. 3. Isothermal annealing of carrier concentration. Reference point of measurement was 77 K. □-sample C before and ■-sample C after remarkable plastic deformation.

The concentration of Ga was $1.4 \cdot 10^{15}$ cm^{-3} (sample A) and $1.4 \cdot 10^{14}$ (sample B). Only one annealing stage between 650 K and 700 K in both crystals was discovered. The carrier concentration at 77 K was completely recovered. The remaining carrier concentration at 300 K belongs to the deeper acceptor level.

Performing the isochronal annealing in the range of 77—300 K a very small variation of carrier concentration at 77 K after each annealing was established.

The results of isothermal annealing are shown in Fig. 3 when the reference point of the measurement was 77 K. The recovery process is well represented by the first-order kinetics. The time necessary for 50% of the annealing to occur is plotted as a function of reciprocal annealing temperature in Fig. 4. From the slope of this curve the activation energy of annealing process is (2.30 ± 0.10) eV. The same value is obtained from the annealing data when 300 K as the reference temperature was used. The annealing rate constant is the same for all the samples independently of the gallium concentration. This rate constant does not depend on the quenching temperature even for the temperature above 900 K when the dislocation density is remarkably increased because of the plastic deformation of the samples[23].

The concentration of thermal acceptors as a function of reciprocal quenching temperature is shown in Fig. 5. The heating of the samples lasted 10 minutes, sufficiently long to reach the saturated value of acceptor concentration[21]. The fraction of carriers induced by quenching was determined at 167 K. It is equal to the concentration of thermal acceptors due to the full ionization of lower acceptor level at this temperature. The concentration of acceptors obeys the Arrhenius relation up to 900 K with an activation energy of (1.00 ± 0.15) eV and it does not depend on the concentration of Ga (Fig. 5, samples A, C and D). The acceptor concentration is larger in thinner samples (samples E, A, D). However, there is a limit of sample dimensions since the plastic deformation occurs at relatively lower quenching temperatures for very thin samples (sample F).

The concentration of defects at temperature above 900 K decreases with increasing temperature tending to be equal for all the samples. This increasing is probably related to the remarkable plastic deformation of the sample. If the plastically deformed samples are again quenched from the temperatures under 900 K, the smaller concentration of thermal acceptors is obtained (sample C). In deformed crystals the acceptor levels are the same, but the Hall mobility is reduced.

4. Discussion

The present experimental results confirm the assumption that the thermal defects introduced by quenching into p-type Ge are not single vacancies. This statement is supported by the fact that thermal defects anneal-out at higher temperatures

(650 — 700 K) with the activation energy of (2.30 ± 0.10) eV, suggesting the complex structure of thermal defects. They are probably divacancies of the associations of vacancies with impurities.

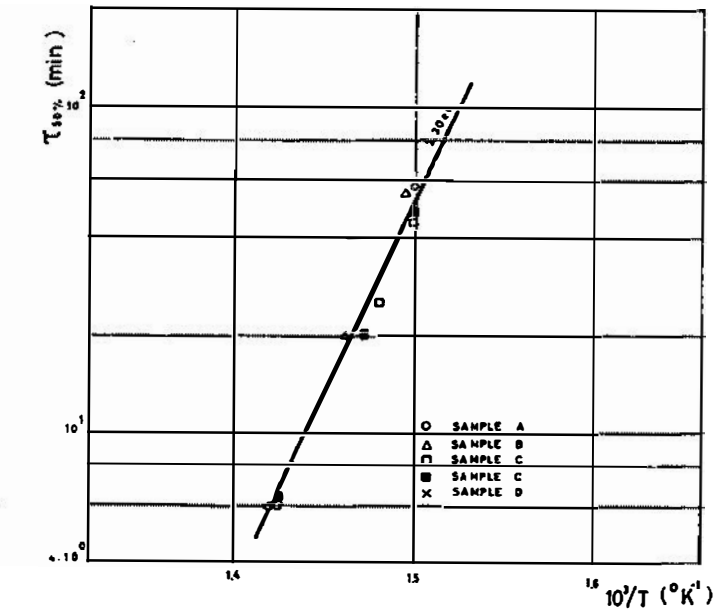

Fig. 4. Time necessary for 50% of the annealing to occur as a function of reciprocal annealing temperature.

The sort of impurity the single-vacancy is associated with is under the question. At the very beginning, gallium as the impurity must be excluded since this experiment shows the thermal acceptor concentration does not depend on the gallium concentration. The concentration of impurity must be higher than the concentration of thermal acceptors, i. e. higher than $6 \cdot 10^{14}$ cm^{-3}. Owing to the high content of oxygen in Ge[1], the complex oxygen-vacancy might be considered. However, it has already been shown that single vacancy-oxygen complex annealed out under the temperature of 300 K[18]. According to these facts, the most of lattice defects quenched in p-type Ge are not impurity-vacancy associations.

The first-order annealing kinetics suggests a rather simple structure of thermal defects. Therefore, consider now the kinetics of the annealing process supposing that the quenched-in defects are divacancies. The annealing process can generally be expressed by differential equations

$$dN_{2V}/dt = K_D N_{2V} - K_v N_{1V}^2, \text{ and} \qquad (1)$$

$$dN_{1V}/dt = 2K_v N_{1V}^2 - 2K_D N_{2V} + (N_{1V} - N_{1V}^0)/\tau_v, \tag{2}$$

where N_{2V} and N_{1V} are the concentrations of divacancies and single-vacancies, respectively; K_D, K_v and $1/\tau_v$ are the reaction rate constants of divacancy dissociation, divacancy generation and single-vacancy precipitation on the dislocations, respectively.

For a regular array of dislocations of the n_D density, the rate constant $1/\tau_v = \beta n_D D_{1V}$, where D_{1V} is the single-vacancy diffusion coefficient and β is a geometrical factor slightly depending on the dislocation density[26].

If the generation of divacancy from two singlevacancies is controlled by their diffusion[27], then the rate constant $K_v = 32D_{1V}/a^2N_L$, where a is the lattice constant and N_L the concentration of host lattice sites.

The system of equations (1) and (2) can be solved introducing some approximations. As the annealing process at the higher dislocation densities does not depend on the dislocation density and according to the high mobility of single-vacancies in the temperature range from 650 to 700 K the following assumptions can be used

$$1/\tau_v \gg K_v N_{1V}^0, \text{ and} \tag{3a}$$

$$1/\tau_v \gg K_D. \tag{3b}$$

It means that the vacancy precipitation process is considerably faster than the other two processes. The approximative solution of equations (1) and (2) under the assumption (3a) and (3b) is

$$N_{2v} - N_{2v}^0 = (N_{2v}^0 - N)\exp(-K_D t), \tag{4}$$

where N_{2v} is the concentration of divacancies after the annealing time t; N_{2v}^0 the equilibrium concentration of divacancies at the annealing temperature and N is the concentration of divacancies at the beginning of the annealing process ($t = 0$).

According to (4) the dislocation rate constant is equal to the annealing rate constant, determined experimentally from the isothermal annealing data as $K_D = 5.5 \cdot 10^{13}\exp(-2.30\,\text{eV/kT})\,\text{s}^{-1}$, where the energy of 2.30 V represents the dissociation energy of divacancy.

The dissociation energy of divacancy is given by $E_{2V}^D = E_{2V}^B + E_{1V}^M$, where E_{2B}^B is the binding energy of divacancy and E_{1V}^M the migration energy of single-vacancy. If the migration energy of single-vacancy $E_{1V}^M = 0.2$ eV, then the binding energy of divacancy in p-type Ge, E_{2V}^B, should be 2.1 eV. This value is considerably larger than the calculated values of 1.03 and 1.14 eV which are closed to the ones found for silicon[28]. However, the annealing experiments of EPR spectra for silicon showed

that the lower limit of E_{2V}^{B} lies approximately at 1.6 eV[29]. In respect to this value, here the obtained binding energy of divacancy might be taken as a reasonable value.

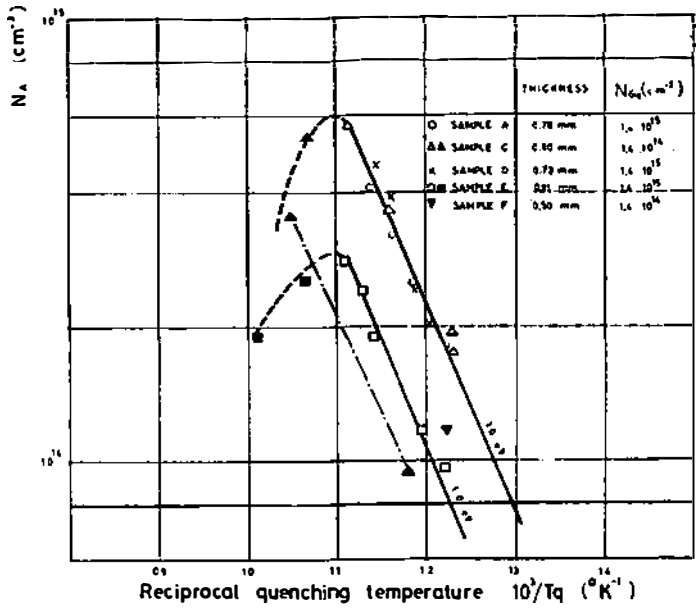

Fig. 5. Concentration of thermal acceptor as a function of reciprocal quenching temperature. △- and □-samples C and E before remarkable plastic deformation; ▲- the same samples after remarkable plastic deformation.

The earlier mentioned decreasing of thermal acceptors concentration above 900 K could be explained with the model described by equations (1) and (2). Supposing that $K_v N_{1V}^0$ or K_D are larger than $1/\tau_v a_c$ temperatures above 900 K, then the effective annealing rate constant increases with increasing the dislocation density. Actually, the remaining concentration of thermal defects will be smaller than the equilibrium concentration at quenching temperature due to the annealing during the cooling of the sample. If this annealing of defects is present at temperatures under 900 K, then the energy of 1.0 eV is an effective energy which is smaller than the actual formation energy. The quantitative conclusions concerning this problem could be done solving the system of equations (1) and (2) for different cooling conditions and performing the experiments with various cooling rates.

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ODGREVANJE TERMIČKIH DEFEKATA U p-Ge

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Sadržaj

Izohronim i izotermalnim odregavanjem proučavani su termički defekti u p-Ge. Otkriveno je samo jedno stanje odgrevanja u opsegu temperature 650—700 K. To ukazuje na visoku stabilnost termičkih defekata. Konstanta brzine odgrevanja, koja ne zavisi od gustoće dislokacije pri visokim gustoćama dislokacija, data je izrazom $5 \cdot 5 \cdot 10^{13} \exp(-2.30\,\mathrm{eV/kT})\,\mathrm{s}^{-1}$.

Proces odgrevanja može se predstaviti kinetikom prvog reda. U interpretaciji eksperimentalnih rezultata pretpostavljeno je da su termički defekti divakancije. Na taj način, akvitaciona energija od 2.30 eV objašnjena je kao disocijaciona energija divakancije. Ako je migraciona energija proste vakansije od 0.2 eV tačna, tada se za energiju veze divakancije u p-Ge dobija 2.10 eV.