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Room Temperature Annealing of γ-Ray Damage in Germanium

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I. Introduction and Background

When solids are bombarded with radiation, electrons may be removed from their orbits, and atoms may be knocked out of their normal lattice positions. In metals and covalent compounds, large changes of properties are induced by the displaced atoms from their lattice sites by collision processes, and the defects produced are primarily interstitial-vacancy pairs called Frenkel defects.

The theory of defect production by high-energy particles has received considerable attention since the prediction of E. P. Wigner[1] in 1943 that extensive radiation effects may be expected in reactor materials. The essentials of the energetics of radiation damage process were first established by Seitz[2] and refined by several investigators[3),4),5),6),7)].

According to Seitz, with the value of 25 eV for the displacement energy, the minimum radiation energy for production of displaced atoms by the various types of radiation may be readily calculated. Results are presented in Table 1.

Table 1. Thereshold Radiation Energy for Displacements with $E_d = 25$ eV (Kinchin and Pease)

Atomic weight of stationary atoms	10	50	100	200
Neutrons; protons (eV)	76	325	638	1263
Electrons, γ-rays (MeV)	0.10	0.41	0.68	1.10
α-particles (eV)	31	91	169	325
Fission fragments (eV)	85	30	25	27

In semiconductors, the irradiation effects can be strikingly demonstrated by the sensitive response of the electrical properties to the introduction of crystal imperfections. Germanium and silicon, being two of the most extensively studied and well understood semiconductors, are therfore suitable materials for investigation.

E. E. Klontz[8] made the experiments of determing the displacement energy of germanium by measuring the resistivity, which he adopted as an index of damage, as a function of energies of the bombarding electrons and extrapolating to zerodamage. The results are shown in Fig. 1 from which it is evident that the threshold energy is 0.63 MeV. This value of threshold energy leads to a displacement energy of 31 eV, which is close to the value of 25 eV.

Loferski and Rappaport[9] have re-examined such measurements on germanium and silicon,

using the minority carrier life time, which is much more sensitive to lattice damage than the change of electron concentration. And they determined a displacement energy of 12.9 eV for both materials.

The changes of conductivity of n-type (electron-excess) and p-type (hole-excess) germanium due to deuteron irradiation are shown in Fig. 2[10]. Measurements of Hall coefficient demonstrate that n-type germanium is converted to p-type by irradiation, and confirm that the irradiation effects are due largely to change in the numbers of charge carriers and not to any changes in mean free path.

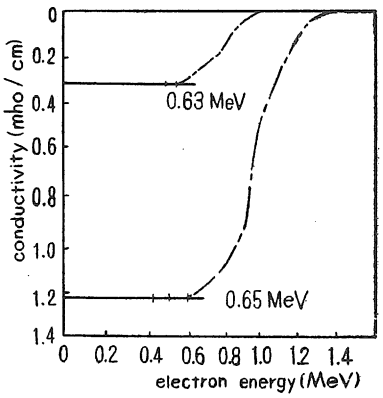

Fig. 1. Conductivity of two germanium samples during electron irradiation as a function of the energy of the electrons (Klontz)

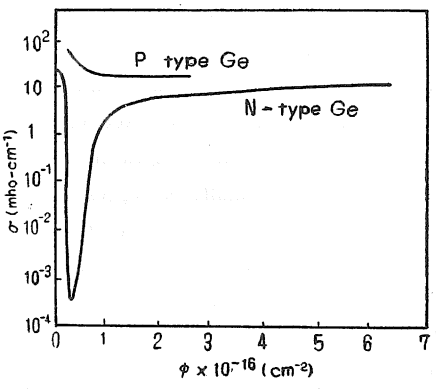

Fig. 2. Change in conductivity of deuteron-irradiated germanium as a function of dose (Fan and Lark-Horovitz)

Hence, we shall be concerned with localized energy states which arise as a result of defects in the diamond lattice. The type of behavior shown in Fig. 2 led James and Lark-Horovitz[11] to propose a model of multiple ionization of both interstitials and vacancies to account for the observed effects of bombardment. They consider that vacancies act as electron traps (sometimes called acceptors) and conclude that each vacancy produces two localized empty levels in the forbidden band as shown in Fig. 3. Similarly interstitials act as donors of electrons (sometimes called hole traps) and each interstitial produces two localized filled levels, also shown in Fig. 3. Another defect energy level models were reported by several writers[10),12),13)] but the James and Lark-Horovitz model seems to be most reliable.

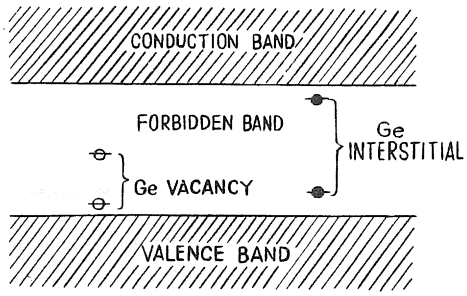

Fig. 3. Energy levels in irradiated germanium (James and Lark-Horovitz)

The tacit conclusion of the preceding was that bombardment introduces Frenkel defects, and it is these with which we shall be concerned while discussing a possible energy level model. However, several writers shows[6),7)] that the damage resulting from massive high-energy particles is not randomly distributed, but rather is better described by regions of high local disorder distributed throughout a more nearly perfect matrix. On the other hand, we expect that the damage caused by electron beam will consist of the simplest form. Furthermore, in the present experiments, the

defects were introduced by Co 60 gamma-rays, since these appear to be caused by the simpler defect distribution.

During radioactive decay Co 60 emits equal intensities of 1.17 MeV and 1.33 MeV photons. The predominant absorption process in germanium for gamma rays of this energy is Compton scattering, which produces Compton electrons throughout the specimen. Since the maximum energy of Compton electron from Co 60 gamma rays is 0.96 MeV[14], it is evident that on the average the energy transferred to the struck atom is not sufficiently large to cause secondary displacements. Therefore, owing to their large range in a solid of the density of germanium, Co 60 gamma radiation is convenient means of producing isolated Frenkel pairs and gives more clearcut results than massive particles.

In most cases, on rising the temperature of a specimen after irradiation the physical properties revert to their former values. Recovery produced by heating usually takes place in several stages, with different activation energies in different ranges of temperature, and the course of a given recovery process can usually be represented by the equation[6]:

$$dn/dt = -cn^{\gamma}exp(-E/kt) \qquad (1)$$

where n is the number of defects taking part in the recovery process, E is the activation energy, c is a constant and γ is often termed the order of reaction by analogy with gaseous chemical reactions.

The presnt experiments deal with the thermal annealing of defects in germanium caused by irradiation of Co 60 gamma rays at dry ice temperature.

II. Experimental Procedure

Specimens about $1\times1\times5$ mm^3 were cut from three single crystal rods of n-type germanium which had initially a resistivity of 8 ohm-cm, 15 ohm-cm and 20 ohm-cm, respectively. In order to determine the dislocation density, the observation of etch pits have been made on crystals which were cut within a (111) plane. All etchants used in this investigation are based on the standard CP-4 etchant whose composition is as follows:

Nitric acid (69%)	50 cc
Acetic acid (100%)	30 cc
Hydrofluoric acid (48%)	30 cc
Bromine	0.6 cc

The specimens were exposed to gamma rays from 1500 Curie Co 60 to a total dose of 4×10^7r at dry ice temperature (-77°C). Irradiation were performed using special facilities which lodged in irradiation waterpool. The details of irradiation facility were illustrated in Fig. 4. The samples were sealed in the evacuated glass tubes and this

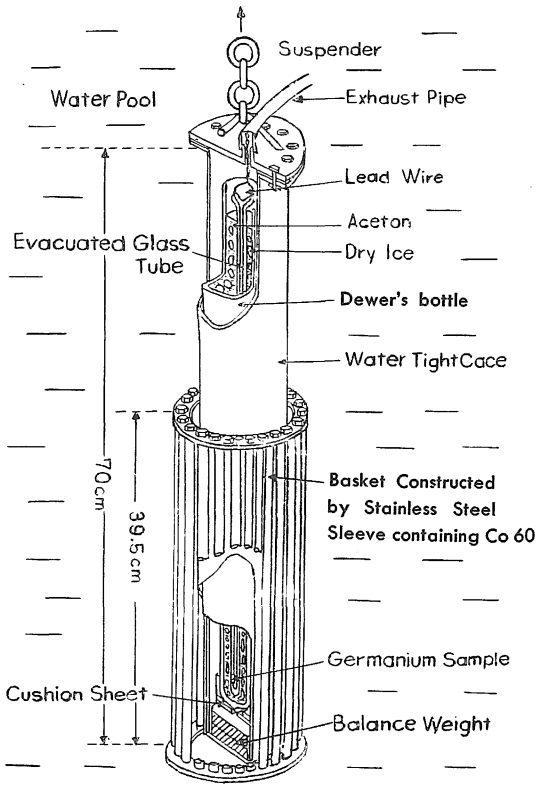

Fig. 4. The details of irradiation facility

mounting remained through complete annealing processes.

After it was confirmed that remarkable resistivity change did not occur during the preservation of the irradiated specimens below $-20°C$, isothermal annealing of these specimens was carried out. The annealing was perfomed in water baths with heating and cooling equipments. The temperature was controlled to $\pm 0.02°C$ above room temperature and to $\pm 0.1°C$ below, covering a range between $0°C$ and $55°C$.

The variation of resistance with time at predetermined constant annealing temperature was measured.

III. Results and Discussion

For the preliminary and major experiments, the rod of resistivity of 15 ohm-cm was selected. The recovery was determined from conductivity measurement. Typical curves showing the relations between the conductance of the specimens and annealing time interval at constant temperatures are shown in Fig. 5.

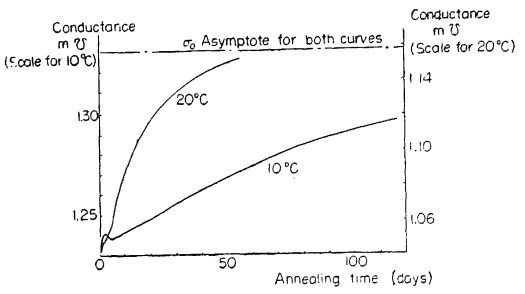

Fig. 5. Conductance of specimens *vs* annealing time

It is well known that the conductance σ is given by the equation:

$$\sigma = ne\mu \qquad (2)$$

where n is the electron concentration in the conduction band, e the electronic charge, and μ the mobility. Since, in the present investigation, the concentration of vacancy-interstitial pairs is estimated to be of the order of 10^{13}/cc from the difference in resistivity before and after irradiation and also the measurements were performed at room temperature range, the change of the carrier mobility due to scattering centers is negligibly small. Therefore, the change of the conductance of specimens should correspond to that of the carrier concentration.

During the course of annealing, Fig. 5 exhibits that the conductance increased at the initial stage, then decreased to a certain value and again increased asymptotically to a final value σ_0. This type of behavior cannot be represented by any simple function. Only a combination of functions will lead to the explanation of the observed annealing behavior. It was found that the last stage of annealing may be represented by $A(1-\exp(-t/\tau_3))$. In order to obtain the time constant τ_3, the values of $\log(\sigma_0-\sigma)$ were plotted against time, σ being the conductance of the specimens during the annealing. The result is shown in Fig. 6 and it can be a fairly good straight line except for the initial stage. On closer examination of deviation from linearity it was concluded that the conductance can be represented as

$$\frac{1}{R} = \frac{1}{R_0} k_1 e^{-t/\tau_1} + k_2 e^{-t/\tau_2} - k_3 e^{-t/\tau_3} \qquad (3)$$

The constants τ_1, τ_2 and τ_3 can be easily estimated by the graphical method. These are plotted as a logarithm of the time constants *versus* $10^3/T$, in Fig. 7. Each straight-line relation shows that the time constants exhibit the temperature dependance of the form

$$\tau_1 \propto \exp(E_i/kT) \qquad (4)$$

with an activation energy E_i.

To explain the fact that the conductance curve consists of three stages Fletcher and Brown's interpretation[15),16)] for annealing process was employed with a slight modification. In n-type

germanium used for our experiments a lattice vacancy can trap two electrons from conduction band and an interstitial atom supplies one to conduction band. Because the defect density is of the

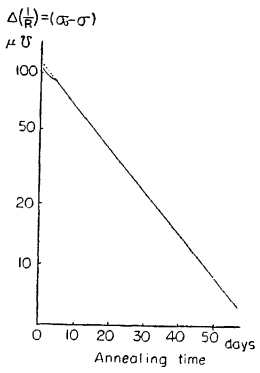

Fig. 6. Plot of $(\sigma_0-\sigma)$ *vs* annealing time

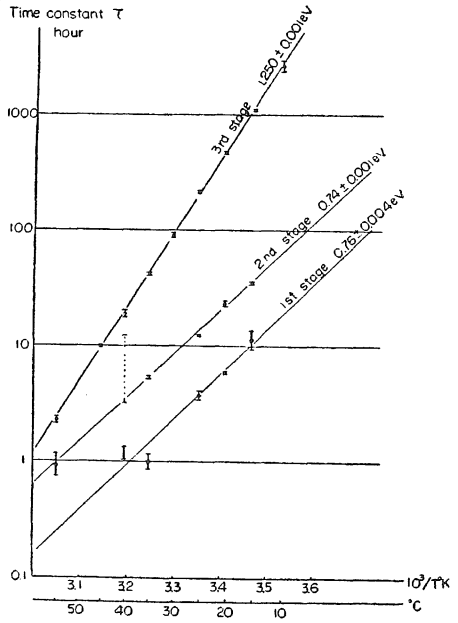

Fig. 7. Plot of τ *vs* 1/T.

order of 10^{13}/cc, it is almost evident that the vacancy-interstitial pairs lie far apart from each other compared with the distance in each pair. When the specimens are heated to an annealing temperature, direct recombination of a vacancy with an interstitial atom in each pair may occur in the first stage. This is simply an annihilation of pairs and the amount annealed may be represented by a simple exponential form with a time constant τ_1.

The so-called "reverse annealing" stage, in which σ decreases with a time constant τ_2, may be considered as follows[7),17),18),19)]. When the specimens are heated, direct recombination may occur as descrived above. One component of the Frekel defects, presumably the interstitial atoms, will begin to diffuse faster than the vacancies, they will wander in the crystal lattice and will finally be annihilated at dislocations or at the surface. This process may have a longer relaxation time than the direct recombination process. When these interstitial atoms disappear at dislocation or at the surface, σ may decrease, because they are acting the role of donors in the crystal.

After the preferential annealing by these mechanisms is over, the vacancies left in the crystal may wander about in the crystal and be annihilated at dislocations or surfaces with a time constant τ_3.

If this model is adopted, analysis of the curves shown in Fig. 7 gives following values for the activation energy for the direct recombination of vacancy interstitial pairs, 0.765 ± 0.004 eV, that for the diffusion of the interstitial atoms, 0.741 ± 0.001 eV, and that for the diffusion of the vacancies, 1.250 ± 0.001 eV.

The conclusion of the preceding led to the same activation energy for the first stage process in the different crystals. However, it is expected that the influence due to the difference from crystal to crystal exerts on the annealing behavior through the second and third stages.

In order to obtain the information of this effects, the experiments are performed using two crystals of different dislocation density. The sample properties are exhibited in Table 2.

Table 2. Sample Properties

Sample number	1	2	3
Number of etch pit per cm^2, (111) face	$\sim 10^2$	$\sim 10^4$	$\sim 10^4$
Initial resistivity (ohm-cm)	20	15	8
Type of specimens	n	n	n
Doping material	?	?	Sb

Annealing curves taken at 25°C for each sample with different dislocation density are shown in Fig. 8 to Fig. 10. There are large difference in the recovery of conductance, whose curves may be

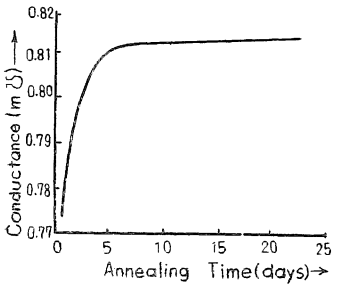

Fig. 8. No. 1 crystal

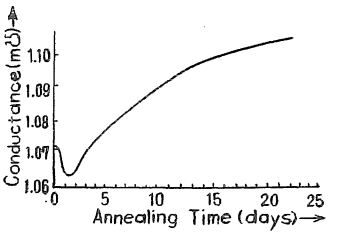

Fig. 9. No. 2 crystal

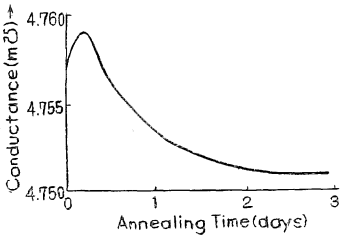

Fig. 10. No. 3. crystal

Comparision of annealing curves for three crystals containing different dislocation density.

explained employing the preceding mechanisms. If the dislocation density is so small as to be absent, the assotiation of interstitials with dislocation will not take place appreciably. Therefore, the conductance may increase successively as shown in Fig. 8.

When the dislocation density was sufficient the "reverse annealing" may appear remarkably. These results are given in Fig. 9 and Fig. 10. The difference of annealing curve between Fig. 9 and Fig. 10 may be attributable to the difference in impurity concentration. Successibly decreasing conductance may be interpreted as follows. The wandering vacancy appears to be associated spatially with chemical donors[20]. Such assotiation could remove two charged impurity centers without changing the carrier concentration.

More experiments along these lines will be necessary to determine the exact nature of the annealing process.

IV. Acknowledgements

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