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A STUDY OF 14-MeV NEUTRON INDUCED DEFECTS IN *p*-TYPE GERMANIUM

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Abstract: Gallium doped germanium samples with initial room temperature resistivities from 2 to 20 Ωcm were bombarded with 14-MeV neutrons at 77°K. The Hall coefficient and the electrical conductivity were measured as a function of neutron fluence. Initial carrier removal rates were determined for a set of samples with different initial hole concentrations, and it was concluded that the limiting Fermi level lies above $E_v + 0.06$ eV.

In isochronal annealing measurements performed from 77°K up to room temperature after irradiations three annealing stages were found: the first between 80° and 160°K, the second between 160° and 260°K, and the third above 260°K. The first stage was attributed to certain rearrangements of defects resulting in the increase of the number of donor centres in the gap. The second annealing stage can be connected with cluster dissociation and vacancy migration. The third stage shows no change either in hole concentration or in mobility.

1. *Introduction*

Defects introduced by fast neutron irradiation in the germanium lattice have been extensively investigated [1, 2] and more attention has been devoted to *n*-type than to *p*-type germanium. Neutrons from a nuclear reactor with a wide range of energies were used in most cases, although experiments with monoenergetic neutrons would be more desirable, as neutrons with different energies give rise to different disordenings in the lattice. The energy transferred to the atoms of the lattice, as well as the type and the spacing of the introduced defects vary with neutron energy. Various defects are possible, such as isolated pairs of interstitials and vacancies, and smaller or larger clusters of defects or disordered regions. Thermal neutrons cause transmutations, which is equivalent to introducing impurities into material. Besides, the presence of β and γ radiation in a reactor is an additional disadvantage of this type of neutron source.

The present work was undertaken to study the behaviour of defects produced by monoenergetic neutron bombardment of *p*-type germanium. Irradiations were performed at liquid nitrogen temperature, and isochronal annealing measurements were carried out in the temperature range from 77° K up to room temperature.

2. *Experimental*

Monoenergetic neutrons were obtained from the D-T reaction by use of a 200-kV Cockcroft–Walton accelerator. Neutrons have an angular distribution of energy from 15.1 MeV in the 0^0 direction to 13.2 MeV in the 180^0 direction towards the incident deuteron beam. Samples were placed 3 cm from the target at a neutron energy of 14.2 MeV. The neutron flux was determined directly by a long BF_3 counter and independently by another counter detecting alpha particles produced simultaneously with neutrons.

The samples were cut from monocrystal ingots of p-type germanium grown by the Czochralski method and doped with gallium having the initial room temperature resistivities in a wide range from 2 to 20 Ωcm. The specimens were shaped in rectangular parallelepipeds with their broad face in the 110 plane and mounted on a plexiglass holder. The Hall coefficient and the electrical resistivity were measured by a standard DC method during bombardment and annealing experiments. Six copper leads connecting the sample to the measuring circuit were soldered with indium solder using a zinc chloride flux that gives good contacts necessary for electrical measurements. These copper leads also keep the sample fixed on the plexiglass holder.

Irradiations were performed at liquid nitrogen temperature. The magnetic field necessary for Hall coefficient measurements during bombardment was obtained from a solenoid with a ferrite core immersed in liquid nitrogen together with the sample. This electromagnet was calibrated by a germanium hallotron. Magnetic fields ranged up to 1500 Gauss. After irradiation the sample with the plexiglass holder was transferred without warming into a cryostat and isochronal annealing measurements were started immediately at this lowest temperature. A deep, liquid nitrogen filled Dewar was employed as cryostat, placed between the poles of an electromagnet. Inside a 30-watt cylindrical heater immersed in liquid nitrogen the sample holder was placed at a fixed position. In this way it was possible to vary the annealing temperature from 77^0 K up to room temperature.

3. *Results and discussion*

3.1. Irradiation. All samples showed a decrease both in hole concentration and in Hall mobility during irradiation. For example, a specimen of the initial hole concentraton $p_0 = 2 \times 10^{14}$ cm^{-3} showed after the neutron fluence of 2.4×10^{12} neutrons/cm^2 a 9% decrease in hole concentration and a 10% decrease in Hall mobility. In order to calculate the carrier removal rate $\frac{dp}{d(nvt)}$ it is necessary to measure the Hall coefficient, i. e. the majority carrier concentration. The initial carrier removal rate is determined for a set of samples with different initial carrier concentrations. The quantity $\left(\frac{dp}{d(nvt)_f}\right)_{\text{initial}}$ is equal to $-12\ \text{cm}^{-1}$ for the sample of lowest p_0 and becomes higher as p_0 increases. It is known that all germanium specimens regardless of their initial type appear to approach a limiting value for the hole concentration p^* after prolonged irradiation. The concentration p^* given by the value of p_0 at which $\left(\frac{dp}{d(nvt)_f}\right)_{\text{initial}} = 0$ corresponds to the limiting value ζ^* of the Fermi level given by $\zeta^* = E_v + 0.123$ eV (for 195^0 K and room temperature irradiations) and seems to be temperature independent, while the limiting value p^* follows from the relation

$$p = 2\,\frac{(2\pi\, m_h kT)^{3/2}}{h^3}\, e^{-\frac{\zeta}{kT}} \,.$$

Assuming also the above value for the level ζ^* at lower temperature, the corresponding concentration p^* at 77^0K should be $\sim 1 \cdot 10^{10}$ holes/cm^3. The rate $\left(\frac{dp}{d(nvt)_f}\right)_{\text{initial}}$ is below zero for $p_0 > p^*$ and above zero for $p_0 < p^*$. Since our samples have $p_0 > 1 \cdot 10^{10}\ \text{cm}^{-3}$, the initial carrier removal rate is negative. From our measurements we can only conclude that the limiting value ζ^* is higher than $E_v + 0.06$ eV. Recent investigations of Konopleva *et al.*[3] show that the limiting value ζ^* lies near the centre of the forbidden band gap if samples are irradiated at low temperatures.

3.2. Isochronal annealing. The typical behaviour of samples irradiated at liquid nitrogen temperature and isochronally annealed from 77^0K up to room temperature is shown in Figs. 1 and 2. Measurements were performed at a reference temperature of 77^0K and the duration of annealing at each temperature was 10 minutes. There are three clearly pronounced annealing stages in the measured temperature range: the first between 80^0 and 160^0K, the second between 160^0 to 260^0K, and the third above 260^0K.

At the first stage we observed the reverse annealing of the hole concentration p which decreases and has a minimum near 160^0K, while the Hall mobility μ_H increases toward the prebombardment value.

At the second stage the hole concentration begins to increase, while the Hall mobility μ_H rises above the prebombardment value. The third stage shows no change either in p or in μ_H.

The first stage, which was also observed in the case of reactor neutron bombardment by Konopleva and Novikov[3], may be explained as the result of a certain rearrangement of defects leading to the increase of the number of

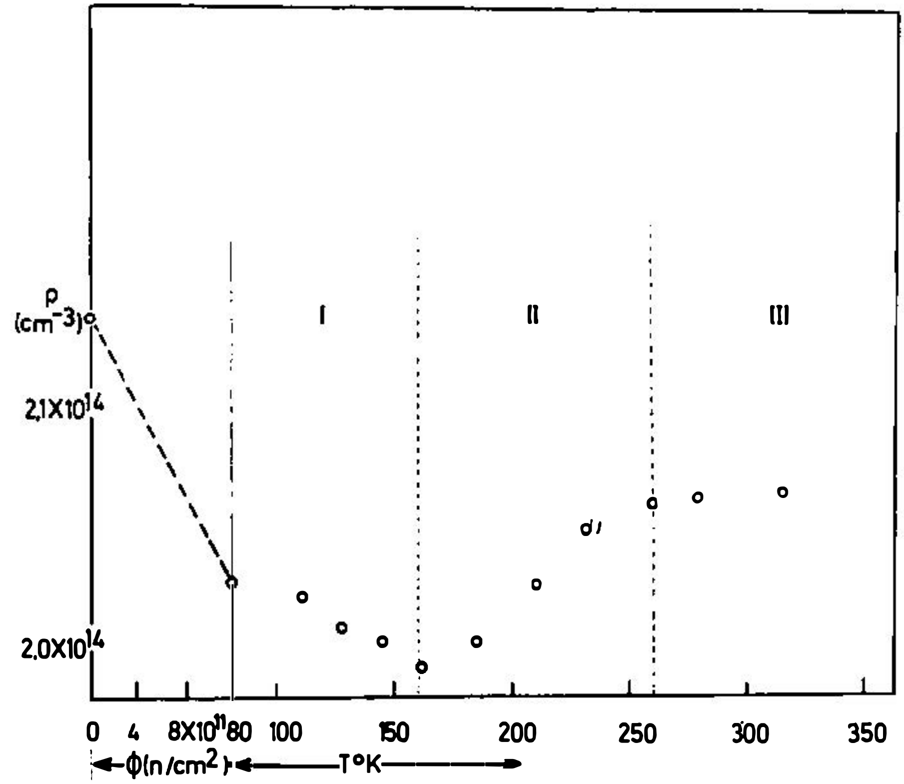

Fig. 1. Ten minutes isochronal annealing after fast neutron bombardment at 77° K: hole concentration behaviour.

donor centres in the gap. The high recovery of the Hall mobility shows that the radiation-induced increase in carrier scattering is removed by this rearrangement of defects. Konopleva and Novikov[3] attributed this stage to some *ripening* of defects, when defect levels were produced rather than eliminated. Swanson[5] also found that in high purity *p*- and *n*-type germanium bombarded by a low dose of reactor neutrons the recovery stage was at 95°K. He assumed that this stage was associated with the clustering of defects into more complex groups or with the formation of defect-impurity complexes, as observed by Watkins[6] for electron-irradiated silicon in this temperature range.

The second annealing stage from 160°–260°K with an increase in *p* shows that the donor centres begin to disappear. Such a monopolar annealing of donors was observed by Konopleva and Novikov[3] in reactor irradiated *p*-type and in *n*-type germanium. This stage might be connected with cluster dissociation and vacancy migration. Whan[7] has concluded from optical absorption measurements that vacancies in *n*-type germanium are mobile at 65°K, while the temperature at which a vacancy moves in *p*-type germanium has not been determined. By analogy to the vacancy motion in silicon at 65°K in *n*-type and at 160°–180°K in *p*-type, the vacancy in *p*-type germanium is expected to migrate at the corresponding higher temperatures near 200°K. Several investigators[8, 9] have observed a significant annealing stage in *p*-type germanium just at 200°K. From 200°K to higher temperature is the temperature range where large disordered regions introduced by heavy particle bombardment start to dissociate into smaller clusters or even into single vacancies or interstitials[10]. However, the vacancies which are liberated from large clusters introduced by fast neutron bombardment will not be stable at higher temperatures and will form vacancy-impurity complexes, as observed by Whan[11] from optical absorption measurements. Our observation of the Hall mobility increase above the prebombardment value after annealing at temperatures above 200°K supports this assumption. This mobility behaviour can be explained by assuming that negatively charged gallium acceptors originally pre-

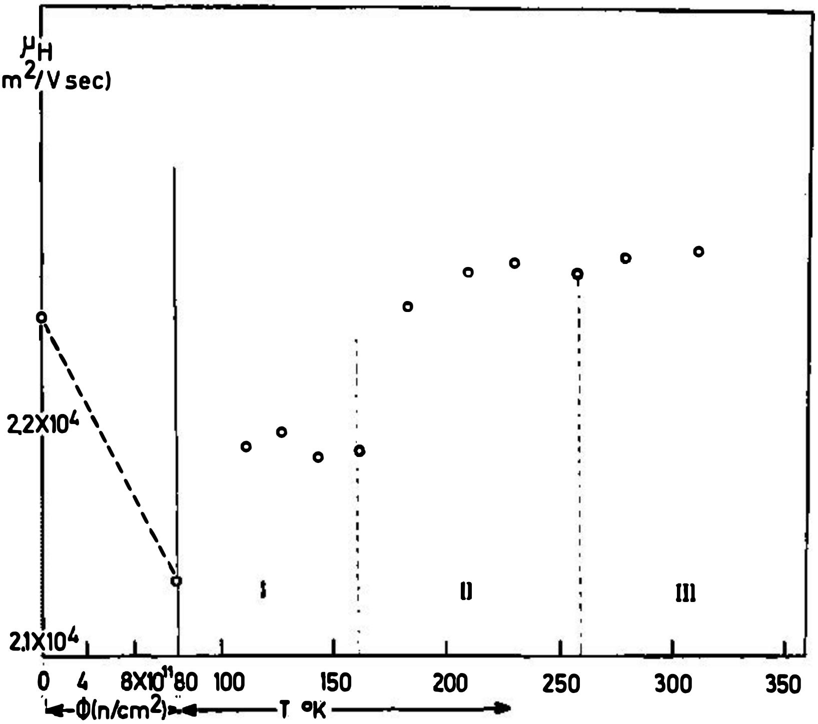

Fig. 2. Ten minutes isochronal annealing after fast neutron bombardment at 77° K: Hall mobility behaviour.

sent in germanium have been associated with radiation-induced positively charged centres, so that the scattering of carriers is smaller after bombardment than before.

Swanson[5)] also reported a significant recovery near 180°K which he attributed to free vacancy migration.

At the third stage (above 260°K) there is no annealing in the hole concentration. Since at 77°K the hole concentration is determined by the ionization of shallow acceptors near the top of the valence band, it follows that such shallow acceptor levels are stable at this annealing stage. As we can see from Fig. 1, the hole concentration at the third annealing stage is still lower than its prebombardment value, i. e. there is a certain defect fraction that is stable in the temperature range of the third stage. At temperatures above 500°K Konopleva and Novikov[3)] have found a practically complete restoration of the hole concentration. So it is reasonable to expect that the stable fraction of the third stage will anneal out at higher temperatures.

The present investigation shows that the annealing of defects introduced by monoenergetic fast neutrons is very similar to the annealing of defects introduced by reactor neutron irradiation. This indicates that the disordered regions which are introduced as defects by 14-MeV neutron irradiation, are also predominant in reactor neutron irradiation and annealing.

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ISPITIVANJE DEFEKATA UVEDENIH NEUTRONIMA ENERGIJE 14 MeV U GERMANIJ *p*-TIPA

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Sadržaj

Ispitivao se je utjecaj zračenja neutronima, energije 14 MeV, iz Cockcroft–Waltonovog akceleratora na električna svojstva germanija *p*-tipa s početnim specifičnim električnim otporima od 2 do 20 Ωcm kod sobne temperature. Ozračavanja su vršena kod 77^0K. Za vrijeme zračenja mjerila se je specifična električna vodljivost σ i Hallova konstanta R_H kao funkcija vremenski integriranog fluksa brzih neutrona. Iz tih mjerenja određivana je početna veličina brzine odstranjenja slobodnih šupljina po upadnom neutronu, $\left(\frac{dp}{d(nvt)_i}\right)$ i iz dobivenih rezultata se je zaključilo, da granični Fermijev nivo ζ^*, koji se uspostavlja s neutronskim bombardiranjem, leži iznad $E_v + 0{,}06$ eV .

Zatim su izvršena mjerenja izohronog napuštanja od 77^0K do nešto iznad sobne temperature. R_H i σ mjerili su se uvijek na temperaturi od 77^0K. Utvrđena su tri stadija napuštanja u tom području, i to: prvi od 80^0 do 160^0K, drugi od 160^0 do 260^0K i treći iznad 260^0K. Prvi stadij se tumači kao izvjesno pregrupiranje radijacionih defekata, čiji je rezultat uvođenje donatorskih stanja u zabranjenom energetskom pojasu, što vodi do reverznog napuštanja koncentracije šupljina p, dok se Hallova pokretnost μ_H počinje oporavljati. U drugom stadiju postoji napuštanje donora a μ_H raste do vrijednosti koja je iznad vrijednosti prije bombardiranja. Vjerojatno je, da je to ponašanje od p i μ_H u vezi s disocijacijom razorenih područja i migracijom šupljina koje nastaju tom disocijacijom. U trećem stadiju još su stabilni plitki akceptori koji se nalaze u zabranjenom pojasu blizu vrha valentne zone. Dobiveni rezultati uspoređeni su s objavljenim rezultatima napuštanja defekata uvedenih zračenjem reaktorskim neutronima, te je nađena velika sličnost.