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VI-10. Investigation of the Nature of Impurity States in CdTe

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The nuclear reaction ^{113}Cd(n, γ)^{114}Cd was used for the creation of relatively simple Frenkel-type defects in *p*-type CdTe. The idea was to study the nature of impurity states in CdTe by changes in electrical and optical properties after thermal-neutron bombardment. High-resistivity *p*-type samples change to low-resistivity *n*-type with the energy state of 0.02 eV below the conduction band which is attributed to cadmium interstitials resulting from recoils. A new 0.09 eV-level above the valence band, observed in unirradiated samples was ascribed to copper impurities. Effects of inhomogeneous distribution of defects and some surface phenomena are also discussed.

§ 1. Introduction

The aim of this work was to demonstrate the possibility of using nuclear radiation, *i.e.* thermal neutrons, as a tool for investigating the nature of impurity states and defect interactions in semiconducting II–VI compounds. Investigations were carried out on CdTe, a semiconductor which also has desirable nuclear properties (a high thermal-neutron absorption cross-section).

The absorption of a thermal neutron is followed by a prompt cascade emission of gamma energy of 9 Mev, and relatively simple Frenkel-type defects are introduced by the recoils of energetic ^{114}Cd nuclei. Oswald and Kikuchi[1] used the same mechanism for the introduction of defects in CdS, and Walker[2] showed that (n, γ) recoil damage could be important in respect to reactor fast-neutron damage even in 32 of the elements.

Electronic properties and impurity states of both *n*-type and *p*-type CdTe have been extensively studied in recent years.[3–5] Although several energy levels have been detected in the forbidden band and their properties described, yet in most cases it has been impossible to assign unambiguously the energy states to the specific type of defects. The difficulties arise from the fact that II–VI compounds are characterized by small deviations from the stoichiometric ratio, and the properties of native defects are obscured by the presence of foreign impurities. Experiments on high-purity *n*-type CdTe were performed by Lorenz, Segall, and Woodbury.[6] They showed that an intrinsic defect acting as a double acceptor was introduced by heat treatment or by electron bombardment.

In this paper the results of a more distinctive way of introducing structural defects in *p*-type CdTe will be presented. By comparing the physical properties of a series of samples of different origin and methods of preparation before and after irradiation with reactor neutrons, it was possible to determine the predominant type of the defects introduced, associated with a specific energy level. Resistivity and Hall measurements together with photoconductivity, EPR, optical transmission, and thermally-stimulated-current (TSC) measurements were performed. The stability of the induced defect configurations at room temperatures was also controlled.

§ 2. Experimental

Two different kinds of *p*-type CdTe crystals were used in the present investigations. The first kind of crystals were those obtained by the Bridgman-Stockbarger method, not intentionally doped, the second were multiply zone-refined crystals. Hall and resistivity samples, approximately $12 \times 2 \times 0.8$ mm^3, were chemically polished utilizing H_2SO_4 and $K_2Cr_2O_7$ solution, and, then, carefully rinsed. As crystals did not undergo heat treatment at elevated temperatures the possible effect of cromium doping[6] was insignificant.

As the samples had undergone multiple measurements and transportation to a reactor, solder connections were abandoned due to a little chance to remain undamaged. A special pressure contact holder with gold contacts was therefore constructed for Hall and resistivity measurements in the temperature range from 77°K to about 320°K. There were also provisions for exciting the samples with a small incandescent lamp mounted inside the cryostat.

Conventional *dc* techniques were used for measuring the Hall coefficient and resistivity as a function of temperature.

A UNICAM spectrophotometer was used for optical studies in the near infrared at room temperature. EPR preliminary measurements were done at a frequency of 9342.1 Mc/ sec at lower temperatures. TSC measurements were performed after photoexcitation at 77°K. Photosensitivity was checked at room temperature and at lower temperatures.

In order to emphasize the effects of thermal neutrons samples were irradiated in a graphite-moderated reactor at the position where the thermal-to-fast neutron flux ratio was approximately 10 to 1. Simple calculations show that in this case the ratio of displacements due to thermal and fast neutrons is at least 20.

In order to separate the effects of fast neutrons from thermal-neutron effects samples with almost identical characteristics were irradiated in pairs with and without 0.5 mm-cadmium thermal-neutron shields. The integrated doses of thermal neutrons, determined by cobalt activation detectors, varied from 4×10^{14} to $1\times10^{16}\,\mathrm{n\,cm^{-2}}$.

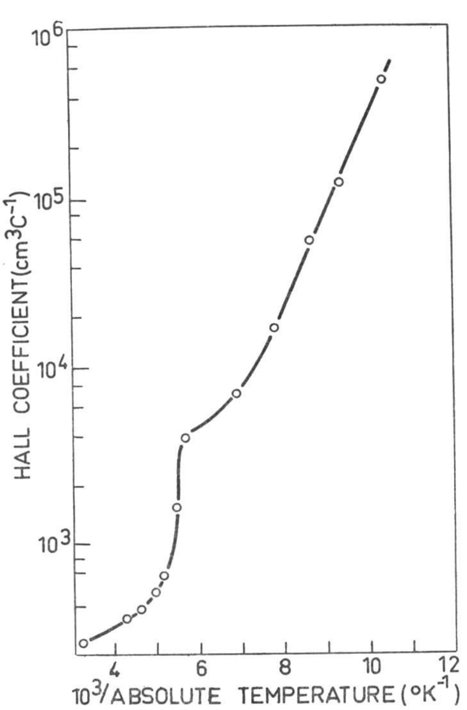

Fig. 1. The R_H vs. $1/T$ curve of one of the multiply zone-refined samples.

The temperature of samples during irradiation did not exceed 50°C.

§ 3. Results and Analysis

Multiply zone-refined samples (series labelled A, B, P) have low resistivity (2 to 10 ohm cm) and mobility between 50 and 100 cm² V/sec.

The Hall data for a sample from these series are presented in Fig. 1. An analysis of the curve, using the expression for compensated semiconductors

$$\frac{p(p+N_d)}{(N_a-N_d-p)}=\frac{N_v}{g}\exp\left(-\frac{E_a}{kT}\right), \qquad (1)$$

where p is the hole concentration, N_d concentration of ionized donors, N_a total acceptor concentration, N_v number of states in the valence band, g statistical factor, E_a ionization energy of an acceptor level, shows that an excellent fitting of experimental values in the whole temperature range is obtained using $N_d=3.6\times10^{16}\,\mathrm{cm^{-3}}$, $N_a=7.0\times10^{16}\,\mathrm{cm^{-3}}$, and $E_a=0.09\,\mathrm{eV}$.

At about 200°K a "step" in the curve is observed. EPR signal of such samples shows a very complex structure, but disappears at temperatures higher than about 200°K. A possible explanation of these effects will be discussed later.

The Hall data for two samples obtained by the Bridgman-Stockbarger method are shown in Fig. 2. (curve 1). They are high-resistivity samples (~2000 ohm cm). Owing to the fact that $p\ll N_d$ in this case, it is possible to simplify eq. (1), and an ionization energy of $E_a=0.35\,\mathrm{eV}$ is obtained directly from the slope of the $\ln R_H T^{-3/2}$ vs. $1/T$ curve.

Results of measurements after irradiation depend upon the initial carrier concentrations, neutron doses, and also on the state of the sample surfaces. There is a significant difference between the effects of thermal and fast neutrons. Samples with the initially low concentration of holes show a change from p-type to low-resistivity n-type at the energy state of 0.02 eV below the conduction band after thermal-neutron bombardment (Fig. 2). The effects of fast neutrons are less pronounced (Figs. 2 and 3).

The state of the sample surfaces should be taken into account for correct interpretation of electrical measurements. Samples which had received more than about $10^{15}\,\mathrm{n\,cm^{-2}}$ showed a blackish surface layer of a few microns of thickness of high conductivity which acts as a shunt

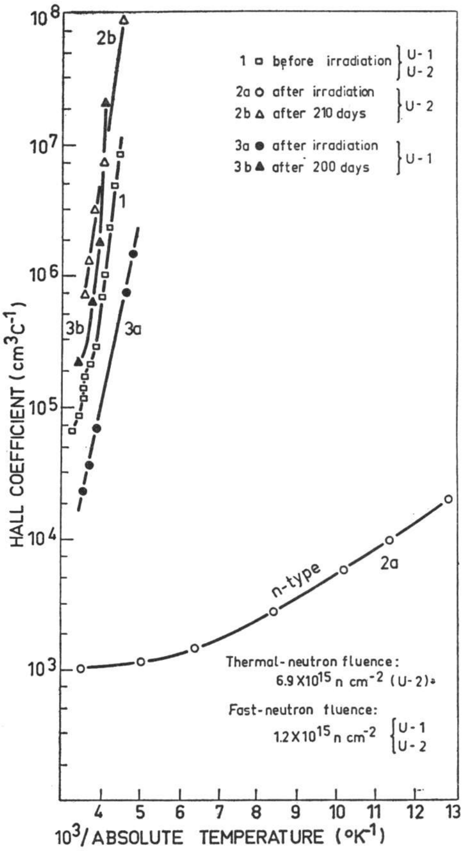

Fig. 2. The R_H vs. $1/T$ curves of two high-resistivity samples before and after irradiation with thermal and fast neutrons. R_H is positive except for the curve 2a. The 2b and 3b curves are obtained after removal of surface layers.

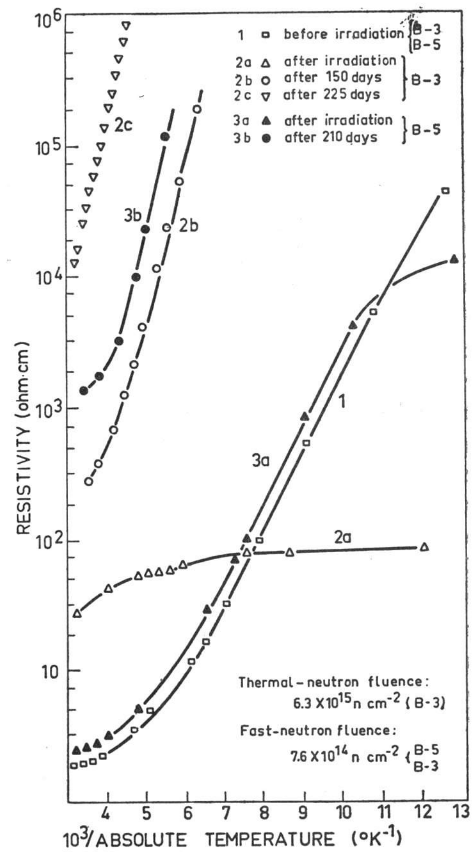

Fig. 3. The temperature dependence of resistivity of the samples B-3 and B-5 before and after irradiation. The 2b, 2c, and 3b curves are obtained after removal of surface layers.

at lower temperatures (Fig. 3. curve 2a). After removing the surface layer a low-temperature plateau disappeared, and resistivity increased. It was of interest to find out the composition of this layer. Monochromatic x-ray studies showed that it is not amorphous but of crystalline structure, and consists of CdO, CdTe, $Cd(CN)_2$, and Cd; neither tellurium nor its oxides were detected. The layer was formed under a combined action of irradiation and atmosphere, during and after irradiation. Spectrographic analysis of surface layers also confirmed that cadmium is present there in excess over the stoichiometric ratio.

Left standing at room temperature after irradiation, all samples show a gradual increase in resistivity and decrease in hole concentrations.

Optical transmission studies show that thermal and fast neutrons introduce absorption at longer wavelengths beyond the fundamental absorption edge; absorption increases with neutron doses. TSC measurements after neutron bombardment indicate a quasi-continuous distribution of energy states in the forbidden band till about 0.50 eV above the top of the valence band. High photoconductivity was detected in fast-neutron bombarded samples at low temperatures.

§ 4. Discussion

Except for the shallower level at 0.05 eV previously attributed to the singly ionized cadmium vacancy[7] in a very pure crystals, the 0.09 eV level, not reported earlier, is closest to the valence band. Using a modified Bohr theory of hydrogen atom and taking into account the dielectric constant, the effective mass, and a screened nuclear charge, Chester[8] has obtained an acceptor level of 0.072 eV above the valence band which is close to our value. The 0.09 eV level is only observed in less compensated crystals; we ascribe it tentatively to a singly ionized copper impurity replacing substitutionally a cadmium atom. (Copper is the main acceptor impurity determined spectrographically in our samples.) The disappearence of EPR signal could be explained in view of paired spins of a doubly ionized defect, and non-equilibrium effects at about 200°K might as well be associated with a lattice relaxation when a negative center accepts a second negative charge.

The 0.35 eV level in more compensated samples is attributed also to copper impurities in accordance with previous reports.[3,7]

Thermal-neutron defects exhibit a donor action compensating for the initially present acceptor states: resistivity increases, hole concentration decreases and p-type samples change to n-type with higher doses. This is in accordance with earlier data.[9]

It should be noted that thermal-neutron defects are not uniformly distributed throughout the bulk because of a high absorption cross-section and flux diminishing inside the samples. The removal of outer layers causes a change from n-type back to high-resistivity p-type samples.

Investigating the diffusion of Cd in CdS Woodbury[10] has shown that cadmium interstitials are immobile parts of Frenkel pairs, and that fast diffusion processes might be explained only by vacancy diffusion mechanisms.

That supports our assignment of the 0.02 eV-level to cadmium interstitials resulting from recoils which are distributed predominantly in the outer layers of the samples and act as donors.[3] x-ray measurements and spectrographic analysis confirm that cadmium is present in excess in surface layers. Vacancy diffusion processes probably change the initial configurations of defects.

Fast neutrons generally introduce disordered regions in semiconductors. Their influence upon the electrical properties of p-type CdTe is not so clear. An increase in hole concentration was detected after irradiation, but the final effect after room temperature annealing and removing of surface layers is also a donor action.

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