PHOTOCONDUCTIVITY AND PHOTOVOLTAIC EFFECT IN THERMALLY TREATED CdTe

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Abstract: A large increase in photoconductivity, the temperature quenching effect, and the appearance of the photovoltaic effect have been observed in thermally treated CdTe in the air up to 450 °C. It has been shown that the introduction of the level $E_c — 0.60$ eV, associated with the cadmium vacancy, is responsible for the enhancement of photosensitivity. Experiments have confirmed that the photovoltage arises due to the inhomogeneities in the distribution of defects in the bulk. Some characteristics of the dynamic behaviour of the photo-emf are also discussed.

1. Introduction

Single crystals of cadmium telluride, as well as many other II — VI binary semiconducting compounds, are particularly susceptible to changes in their physical properties due to various thermal treatments. Depending upon the temperature and the partial pressure of one of the components, it is possible to obtain either n- or p-type crystals due to the departure from the stoichiometric ratio[1]. This process is connected with the diffusion of point defects (vacancies or interstitials) into the bulk of the crystals.

On the other hand, the heating of the crystals in the air at elevated temperatures causes the appearance of low-resistivity p-type surface layers[2]. This process was used for the fabrication of p-n junctions in CdTe[2, 3].

Our primary intention was to make some types of photodetectors from CdTe by the above method. To make ohmic contacts to p-type CdTe samples, after the condenser discharge through the contacts, we heated the samples up to 450 °C[4]. In such a way the ohmic contacts were obtained, but, in addition, the samples showed an enormous increase in photosensitivity. Another interesting result was the appearance of the photovoltaic effect.

The purpose of this paper is to present the results of our investigations of the physical basis of such an increase in photoconductivity as well as to discuss the origin of the observed photovoltaic effect in CdTe.

2. Experimental

All the samples of CdTe used in the present investigations were cut out from the same monocrystal ingot obtained by the zone-levelling method. They were supplied with soldered indium contacts which showed an ohmic behaviour after a condenser discharge followed by a mild heating (up to 150 °C). The resistivities of the samples ranged from 2 to $4 \cdot 10^3$ Ω-cm and the relative photoconductivities $\Delta\sigma/\sigma$ were about 40 percent at room temperature.

In order to find the exact temperature of the onset of the increased photosensitivity, the samples were given 45 minutes heatings in the air between 200 °C and 450 °C (in five steps, increasing the temperature by 50 °C).

A lower resistivity (100 Ω-cm) low photosensitive p-type sample (E-3) of different origin was supplied with gold contacts and subjected to the same thermal treatment. The sample served for comparison with higher resistivity samples.

The resulting changes in the electrical properties of the samples and their stability after heating were monitored by several experimental methods: the temperature dependence of conductivity, the photoconductivity versus temperature and light intensity and the dependence of photoconductivity upon the wavelength of the incident light.

The dynamic and static characterestics of the photoconductivity of the samples and the plotovoltaic effect were measured by a high-imput impedance Keithley electrometer and plotted on a Honeywell x-y recorder.

In order to check the homogeneity of the samples as well as to find out the possible origin of the photovoltaic effect observed in some samples, the exit slit of the prism monochromator was supplied with a microscope objective reducing the monochromatic light beam to a spot of 0.5×0.25 mm^2 in area. That was sufficient to check the spatial distribution of the photosensitivity of the samples with typical dimensions of $6 \times 3 \times 0.5$ mm^3, mounted on an x-y sliding carriage.

In order to distinguish between the surface and bulk properties, the photosensitivity of the samples was also checked after gradual removing of the surface layers in a calibrated etching solution, which consisted of 30 volume parts of H_2SO_4 and 70 volume parts of $K_2Cr_2O_7$. The initial speed of etching was 2 μ/min.

3. Results

The main characteristic of the starting material is the presence of an energy level at 0.20 eV above the valence band[5], as revealed by Hall coefficient measurements and also calculated from the slopes of curves 1 and 2 in Fig. 1 of a typical sample after the thermal treatment. Those curves, taken in the dark, show the existence of a deeper level (or levels) in the lower part of the forbidden gap. Curve 3, taken in the light, shows an enormous increase in photosensitivity at low temperatures. Curve 4 shows some modifications in photoconductivity of the sample aged at room temperature for 5 months.
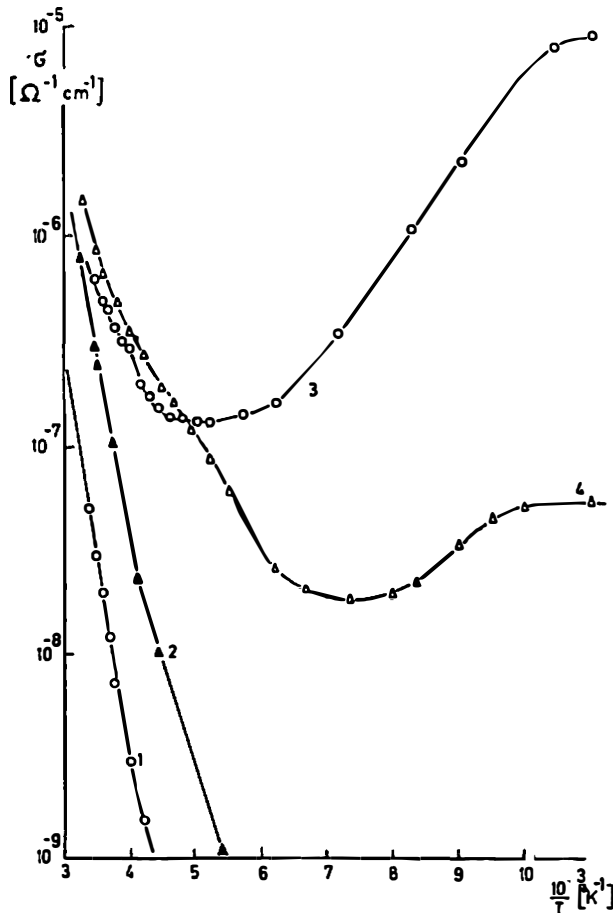

Fig. 1. Temperature dependence of conductivity of a typical sample after thermal treatment. (Curves 1 and 2 taken in the dark, curves 3 and 4 taken in the light). Curves 2 and 4 were taken after the room temperature annealing of 5 months.

In the measurements described it was possible to use an incandescent lamp as a light source owing to the fact that the samples showed photo-sensitivity only in a very narrow spectral region around the absorption band edge[5] (between 0.82 μ and 0.96 μ where photoresponse decreases to 5 % of the maximal value).

Varying the light intensity by neutral density optical filters, a set of photo-conductivity versus minimum in photoconductivity (as the one shown in Fig. 1) shifting toward lower temperatures with decreasing light intensity.

By plotting σ_{min} vs. $1/T$, as suggested by Bube[6], a straight line was obtained with a slope giving the energy of the localized photosensitizing defect level at $(0.5 + 0.1)$ eV below the conduction band[4]. This level is responsible for the low temperature behaviour of the photoconductivity curves.
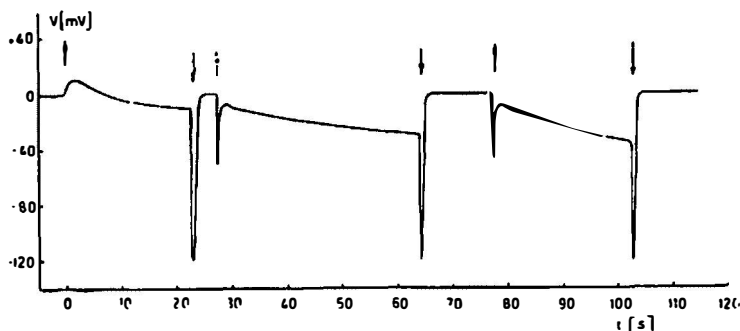

Fig. 2. Dynamical behaviour of photovoltage at room temperature of a thermally treated sample at 300 °C (↑ turn-on, ↓ turn-off of the light).

The effects of the heat treatment were as follows:

1. The heating at 200 °C left the photoconductivity of the samples unchan-ged. The photoconductivity decay curves showed fast and slow time compo-nents. However, the photovoltaic effect was here detected at a much lower heating temperature than in preliminary measurements[4]. In fact, one of the samples showed a small plotovoltage even before heating.

2. After the thermal treatment around 300 °C a change in polarity and a gradual increase in photovoltages was observed after the turn-on of the light. A sharp increase followed by a fast decay of the photovoltage after the turn-off and turn-on was also observed (Fig. 2).

3. A heat treatment at 400 °C led to a large increase in photovoltages with a very fast, almost square-wave on-off response to the light.

4. After heating at 450 °C there were no more time changes in sign of photovoltages, a large increase in resistivity occurred (up to 10^7 Ω-cm), and the photoconductivity increased further ($\Delta\sigma/\sigma \sim 600$ % at room temperature), but the photoresponse became slower.

5. All samples showed gradual changes in properties (for instance, increase in photoconductivity) left standing at room temperature after each step of the thermal treatment.

It is interesting to note that the control, low-resistivity sample behaved differently in many respects in comparison with the high-resistivity samples after the thermal treatment. It should also be mentioned that the control sample was cut from a single crystal of a better quality and homogeneity than the others. The sample showed a large initial increase in photoconductivity ($\Delta\sigma/\sigma \sim 80\%$) even after heating at 200 °C associated with an increase in resistivity (by a factor of 4). However, it is significant that there was no photovoltaic effect in the sample even after heating at 450 °C. The only effect of heating at higher temperatures was an increase of slower components in the photoconductivity decay curves.

The etching test after the thermal treatment confirmed that the induced changes in photosensitivity were due to the variations in the bulk properties. In most samples there were no changes in photosensitivity after removing the surface layers even up to the depth of 50 μ.

4. Discussion

As stated earlier, one of the aims of the present investigations was also to find out the origin of the large increase in photoconductivity of CdTe after the thermal treatment. Fig. 1 shows that the photosensitivity reaches its maximum at lowest temperatures. At higher temperatures it starts to decrease. This is the well-known effect of temperature quenching of photoconductivity. After reaching a minimum, photoconductivity increases again near room temperatures.

Let us try to explain qualitatively such a special behaviour of photoconductivity. For this purpose it is necessary to assume the existence of at least three types of defect centres. The first, designated by I, have an energy level somewhere below the middle of the forbidden gap; the second (type II) have a level about 0.60 eV below the conduction band (as the one found in our measurements), and the third (type III) are characterized by an acceptor level at $E_v + 0.20$ eV, which exists in p-type samples even before heating. It is worthwhile to point out that the decrease in the concentration of this level after the thermal treatment is responsible for a large increase in resistivity (up to four orders of magnitude at room temperature). The temperature behaviour of photoconductivity will depend upon the concentration of those defects and the position of their energy levels in the forbidden energy gap. It is also useful to use the so-called demarcation level in order to distinguish between the trapping or recombination action of defects. We may say approximately that the localized energy levels lying between the

hole and electron demarcation levels will behave as recombination centres, and those outside them, i. e. near the allowed bands, will behave as traps for charge carriers. The positions of the demarcation levels in the gap depend also upon light intensity and temperature.

At high temperatures (or low light intensities) the electron demarcation level will be below the energy level of the type II centres. Then, those centres will act only as electron traps and will not contribute to photosensitivity. However, with decreasing temperature (or with increasing light intensity) the electron demarcation level will be shifted above the level of the type II centres converting them into recombination centres. This will substantially increase photosensitivity because the lifetime of electrons trapped into the II centres before recombination is much longer than that of electrons trapped into the I centres. The result of that dynamic process is that most of electrons are transferred from the I centres to the II centres via the valence and conduction bands by the action of the light. Since the holes are left predominantly in the I centres, their capability as recombination centres is decreased and, therefore, the lifetime of free holes and photosensitivity are increased.

For a constant light intensity, at lowest temperatures, the recombination rate is higher than the speed of the thermal release of electrons from the II centres. This is the region of highest photosensitivity.

For intermediate temperatures the second process starts to grow, and the demarcation level goes below the II centre level — photosensitivity starts to decrease, and this is the region of temperature quenching of photoconductivity.

For higher temperatures the thermal release of holes from the III centres predominates, and conductivity increases again.

From the comparison of the experimental value of the photosensitizing energy level E_c — (0.5 ± 0.1) eV with the values found in literature, we conclude that it corresponds to the doubly ionized cadmium vacancy (usually quoted at E_c — 0.60 eV). Such defects have already been found in CdTe by de Nobel[7] after heating at elevated temperatures.

The decrease in photosensitivity at lower temperatures (curve 4, Fig. 1) after room temperature annealing could be attributed to the decrease in concentration of the E_c — 0.60 eV centres associated with a simultaneous increase in concentration of E_v + 0.20 eV centres (as seen from curve 2, Fig. 1). This would suggest that the cadmium vacancy transforms gradually into a more complex defect by association with an impurity atom, for example.

The second aim was to find out the origin of the photovoltaic effect. First, the possibility of the existence of the potential barrier photovoltaic effect was checked. This situation usually occurs during illumination of the poten-

tial barrier dividing a metal contact and a semiconductor. Since the photo-
voltaic effect in our experiment still existed after the masking of the contacts,
the possibility of the photovoltaic effect originating from the potential
barrier was discarded. Also the etching of the surface layers proved that the
photovoltage was not connected with the surface barrier.

As the p-n junction did not exist in the p-type single crystals used, the
only possible explanation of the photovoltage was the occurrence of the
bulk photovoltaic effect. This effect is due to inhomogeneities in the distri-
bution of impurities and is proportional to the spatial gradient of resistivity.
Indeed, the constant slit illumination with the monochromatic light showed
changes in magnitude and in polarity of the photovoltages along the samples
lengths (Fig. 3). This reflects the magnitude of the changes in resistivity at a
particular portion of the sample and is an exceedingly sensitive method for
checking the crystal homogeneity[8]. The non-existence of the photovoltages in
the control sample even after heating confirmed the better quality and
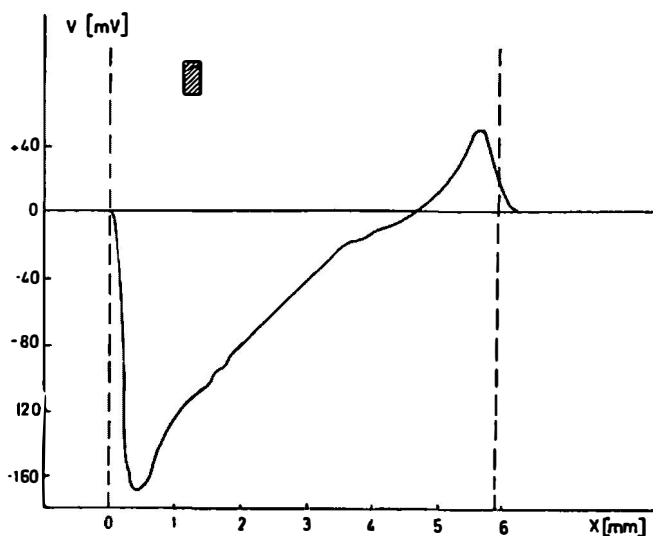homogeneity of that kind of CdTe crystals.

Fig. 3. Spatial dependence of photovoltage of a typical sample illuminated with
the monochromatic light of 0.88 μ. The shaded area represents the magnitude of
the light spot. The broken lines are the positions of electrical contacts.

The overall effect of heating high-resistivity crystals was to enhance the
magnitude of local bulk inhomogeneities giving rise to the appearance or
enhancement of the bulk photovoltaic effect.

It was possible to distinguish several phases in the behaviour of the sam-
ples subjected to the thermal treatment.

The heating treatment at 200 °C in the air causes primarily the surface trapping effects, thus enhancing the slow component in the time decay photo-conductivity after pulse excitation. This treatment is not very effective in the introduction of the sensitizing centre (E_c — 0.60 eV).

Intermediate heating temperatures introduce some peculiar effects in the dynamic behaviour of the photovoltage (Fig. 2). First, we see »flashes« in the photovoltage after the turn-on and turn-off of the incandescent light. The reason for their appearance is not quite clear. One of the possible explanations is to attribute them to the majority carriers generated under transient conditions. In this case the sample should be inhomogeneous and the conditions for recombination and diffusion different in the interior layers from those in the surface layers of the sample. As a result, the establishment of the photo-emf in the interior and in the surface layers requires different time thus making possible the observation of photo-emf »flashes«.

The gradual change in magnitude of the photo-emf with illumination could be associated with the induced impurity photo-emf due to the so-called »optical charge exchange« between impurity levels[9]. In our experiment we used a »white« light source of wavelengths necessary for transitions from the impurity levels. In addition, the presence of deep multiply charged levels is favorable for the observation of such an effect at room temperatures.

The real situation is even more complicated due to the geometrical arrangement: the light falls perpendicular onto the length of the sample and not through one of contacts; this arrangement is more suitable for photoconductivity than for photovoltaic measurements.

The practical result of the investigations performed was the determination of the optimal temperature range (350 — 400 °C) for the photosensitization of the CdTe material, which is suitable for the production of infrared detectors.

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FOTOVODLJIVOST I FOTOVOLTAIČNI EFEKT
KOD TERMIČKI OBRAĐENOG CdTe

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S a d r ž a j

Opaženo je veliko povećanje fotovodljivosti, pojava efekta temperaturnog gašenja fotovodljivosti, kao i javljanje fotovoltaičnog efekta u monokristalima kadmijevog telurida, koji su grijani na zraku do temperature od 450 °C. Pokazano je da se grijanjem uvodi energetski nivo E_c — 0.60 eV, koji je pridružen dvostruko ioniziranoj praznini kadmija i koji je odgovoran za veliko povećanje fotoosjetljivosti.

Diskutiran je model koji objašnjava efekt temperaturnog gašenja fotovodljivosti. Eksperimenti su pokazali da do pojave fotovoltaičnog efekta dolazi zbog nehomogenosti u distribuciji defekata u volumenu kristala i da on nije povezan s površinskim ili kontaktnim efektima. Diskutirane su i neke dinamičke karakteristike opaženog fotovoltaičnog napona.