STABILITY OF GALVANOMAGNETIC PROPERTIES OF CdTe
IN THE RANGE 30 – 100 °C

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Abstract:

The thermal stability of p-type CdTe crystals by using conductivity and Hall-effect measurements have been studied at room and slightly increased temperatures. Different types of thermal relaxation were observed for two p-type samples, which differed in the character and in the rate of the relaxation.

INTRODUCTION

Good thermal stability of semiconductors represents a key demand for fabrication of electronic devices at any application. This also stands for CdTe, which is widely used in photovoltaics and as gamma- and x-ray detectors. The presence of fast diffusing impurities is an often problem for fabrication of electronic devices and their long-term stability at room and slightly elevated temperature. Their elimination is a permanent goal in this field [1].

There are only a few literature data related to the thermal stability of CdTe crystals. Measurements of the Hall effect and electrical conductivity in the range of about room temperature to more than 100°C were studied in semi-insulating p-type CdTe:Cl crystals, where anomalous increase of the resistivity was observed [2]. Another measurements of electrical properties in the range from 295 to 430 K were carried out for semi-insulating p-CdTe:Cl crystals wherein anomalous changes of electrical properties in the range 340 to 380 K were found out [3]. This anomaly was interpreted as the relocation of Cu atoms in the lattice of CdTe. The activation energy of this process was determined from the temperature dependence of relaxation time as 0.87 eV.

In this work we report on measurements of galvanomagnetic properties of different p-type CdTe samples with the characteristic resistivity of $\sim 10^2$ Ω.cm. Classical Hall-bar configuration was used while varying temperature slightly above room temperature 30–100℃. The relaxation of the resistivity in time and the evolution of carrier mobility and concentration after step-like change of temperature are studied. The diffusion coefficient of impurities responsible for the relaxation is estimated and compared with accessible literature.

EXPERIMENT

CdTe crystals were grown in the Institute of Physics of the Charles University by the Vertical-gradient freezing method. Single-crystalline samples were cut from the CdTe ingot. Samples were high-quality intentionally undoped p-type single crystals with hole mobility close to published data [4]. Bar-like samples with the resistivity in the range from 200 to 400 Ωcm and typical dimensions of 3x2x15 mm³ were used in our investigation.
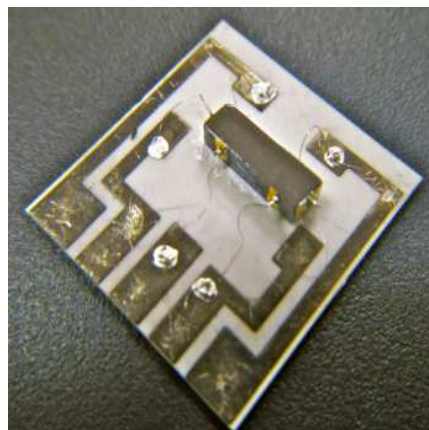

Fig. 1: CdTe sample on a contact pad

The samples were ground, polished, and etched to remove a damaged layer from the surface caused by cutting. Implementing an etching procedure, the surfaces of the sample were treated in bromine-methanol solution and afterwards cleaned in methanol and acetone. After the etching process, the samples were covered by a photoresist in order to form six contacts. The photoresist material was then hardened at 60°C for a period of 20 min. This step was followed by the contact preparation process. The masked sample was immersed into $AuCl_3$ solution to create chemically-deposited Au contacts on the uncovered portions of the sample. After the chemical deposition, the photoresist mask was removed by a lift-off technique in acetone. To finish the contact preparation, silver wires with a diameter of 50 µm were soldered by indium to the Au contacts. The samples were then fixed to a sapphire pad (Fig. 1) and put into a cryostat, wherein temperature dependences of the galvanomagnetic properties were measured. The applied magnetic field was set to 1T. The temperature was controlled by a temperature controller, which enabled us to set a ramp rate of

1 K/min during the experiment. The accuracy of the temperature controlling was approximately 0.1 K.

The measurement of the carrier concentration, electron/hole mobility, and conductivity was carried out with the classical method setup. For this method, four voltage probes are considered, which are divided in pairs on the two lateral sides of the sample. Further, two current contacts are located on the front and back side of the sample, more particular from Fig. 2.
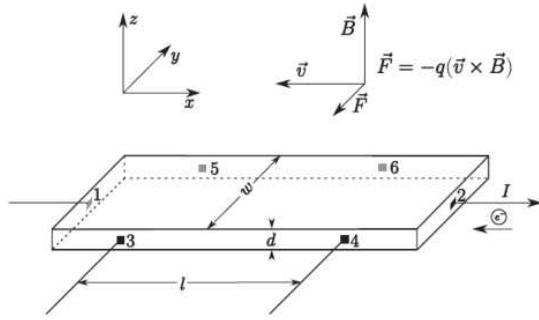

Fig. 2: Classical arrangement for the Hall-effect measuremnts

For the above configuration, while the current flows from contact 1 to contact 2 and the magnetic field B is non-zero, the potencial change E_Y along axis y can be described as follows:

$$E_Y = R_H B_Z J_X \qquad (1)$$

The Hall coefficient R_H is defined as [5]:

$$R_H = -r_H \frac{n\mu_n^2 - p\mu_p^2}{e\left(n\mu_n + p\mu_p\right)^2} \qquad (2)$$

Wherein, n and p are the electron and hole concentrations; μ_n and μ_p are the electron and hole mobilities; e is the elementary charge of the electron and r_H is the Hall factor, which is approximately 1 for our measurements. For the cases where we can neglect one type of the carriers we get a simpler equation:

$$R_H = -r_H \frac{1}{ep} \qquad (2.1)$$

That is, the Hall coefficient is inversely proportional with the concentration of the charge carriers (i.e. holes in our case).

For measuring the conductivity, we use the following equations:

$$\sigma = \frac{1}{\rho} = \frac{l}{dw}\frac{I_{1,2}}{U_{3,4}} \qquad (3)$$

$$\sigma = \frac{1}{\rho} = \frac{l}{dw}\frac{I_{1,2}}{U_{5,6}} \qquad (3')$$

That is, we replace in the above equations l, d and w with the actual length, width, and thickness of the sample. The current measured between contacts 1 and 2 and potential change measured between contacts 3 and 4 (or 5 and 6) with the aforementioned dimensions will enable us to get the conductivity of the sample.

For measuring the carrier concentration, or rather the Hall coefficient, we use the following equations:

$$R_H = r_H \frac{d}{2B}\frac{U_{5,3}^{B^+} - U_{5,3}^{B^-}}{I_{1,2}} \qquad (4)$$

$$R_H = r_H \frac{d}{2B}\frac{U_{6,4}^{B^+} - U_{6,4}^{B^-}}{I_{1,2}} \qquad (4')$$

Thus, we measure the potential change between the two facing voltage contacts 5 and 3 (or 6 and 4) while turning the magnetic field on and changing the polarity of the magnetic field. Deviations of σ and R_H evaluated by the relations (3), (4) and (3'), (4'), respectively, allowed us to eliminate an experimental error.

RESULTS AND DISCUSSION

As apparent in Figs. 3, 4 for Sample I and in Figs. 5, 6 for Sample II, which depict typical parts of the measuring cycle, the measurements consisted in the monitoring of the transport properties of the samples at the temperature steps.
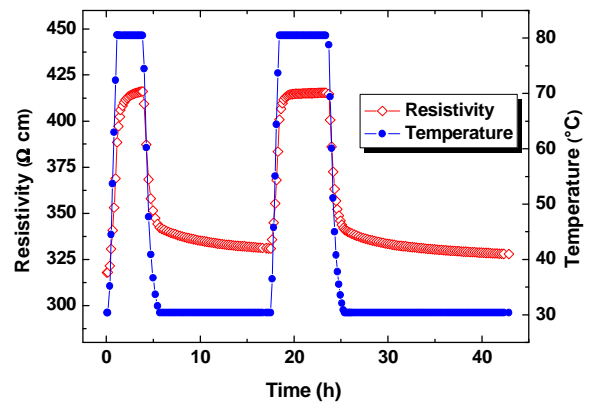

Fig. 3: Example of the resistivity evolution of Sample I at the temperature profile 30°C-80°C-30°C-80°C-30°C
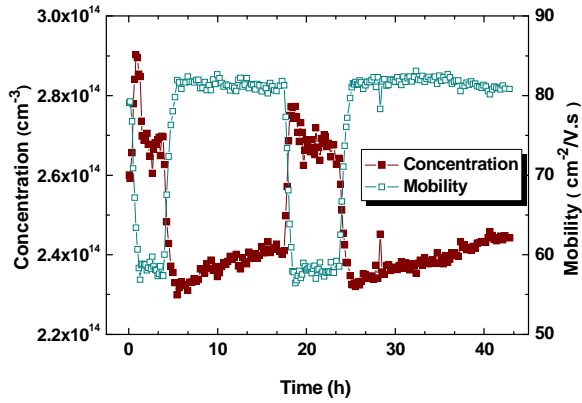
Fig. 4: Example of hole concentration and mobility evolution of Sample I at the temperature profile 30°C-80°C-30°C-80°C-30
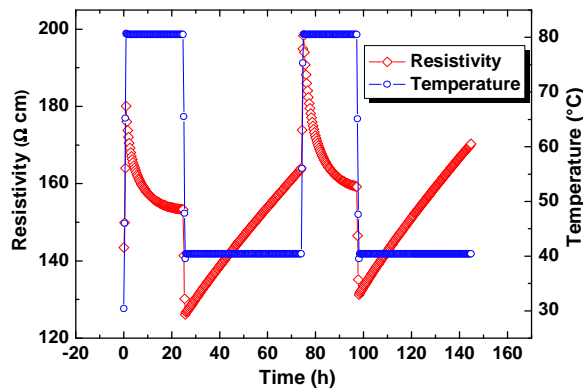

Fig. 5: Example of the resistivity evolution of Sample II at the temperature profile 30°C-80°C-40°C-80°C-40°C
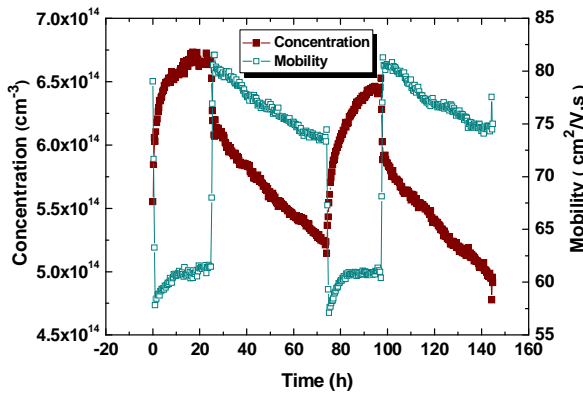

Fig. 6: Example of the hole concentration and mobility evolution of Sample II at the temperature profile 30°C-80°C-40°C-80°C-40°C

In all figures, we may identify two characteristic features of the transport coefficient evolution.

During the temperature changes - increase/decrease - we observe the parallel evolution of the resistivity. The increase of resistivity with raising temperature is unusual in semiconductors and it is explained by the damping of carrier mobility together with minor increase of free carriers density. This effect is often observed in low resistivity CdTe.

After the temperature stabilization, few days evolution of transport characteristics is observed in both samples. While in Sample I we clearly see that the resistivity increases/decreases after the temperature step up/down, just an opposite behavior is identified in Sample II, where the temperature step up/down entails the resistivity decrease/increase.

Thus, for the same type of p-type CdTe samples we observed different behavior of the resistivity relaxation.

As seen in Fig. 4, the hole mobility was constant during the relaxation, and the hole concentration was increasing in the lower temperature and decreasing in the higher temperature in Sample I. In Sample II the mobility was slightly saturating in the higher temperature interval and, as seen in Fig. 6, slightly decreasing in the lower temperature interval. The hole concentration had similar characteristics as the mobility temperature dependence, except that in the lower temperature interval the decrease was more rapid.

The characteristic time of the relaxation varies from few hours at maximum temperature, as we can see in Figs. 3 and 4, up to weeks at minimum temperature, apparent in Figs. 5 and 6. For both samples we carried out the relaxation procedures with different lower temperatures. Since the relaxation of Sample I was relatively fast, we have succeeded to grasp principal part of the relaxation curve, which enabled us to find out an activation energy of the relaxation process and to estimate the diffusion coefficients of the relaxations assuming a diffusion between the sample bulk and surface responsible for the relaxation [6].

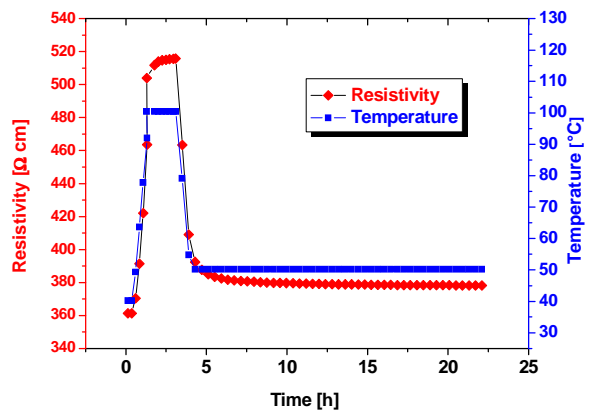Evaluation of the diffusion coefficient D of the sample I is depicted in Fig. 7.

Fig. 7: The resistivity evolution of Sample I at the temperature region 100-50°C

The above graph shows a typical behavior of Sample I and it's resistivity relaxation. As already said the fast relaxation of Sample I allowed us to determine the diffusion coefficient and the activation energy of the process. The diffusion coefficient D is determined by the fit of conductivity via the form [6].

$$| \sigma(t) - \sigma_{\infty} | \sim \exp\left(-\frac{Dt\pi^2 \left(w^2 + h^2 \right)}{w^2 h^2} \right) \qquad (5)$$

The conductivity fit of the relaxation is illustrated on the following figure 8. The solid line in the graph represents the fit of the left side of equation (5). In the equation (5) w and h refer to the cross-sectional dimensions of the sample (width and height) and t represents the time.
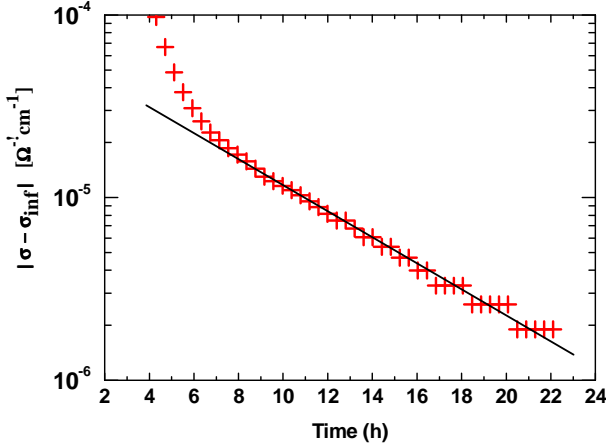

Fig. 8: The evaluated conductivity from the resistivity evolution of Sample I at the temperature range 100-50°C

Analogous evaluations were carried out in order to obtain the activation energy.

As it is apparent in Fig. 9, the corresponding diffusion coefficients were well aligned, thus we were able to determine the activation energy of the relaxation for Sample I to about 0.3eV.
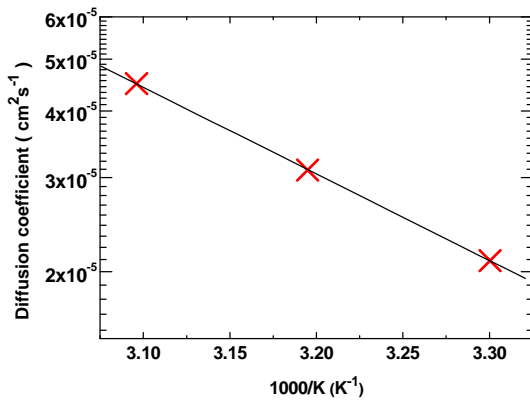

Fig. 9: Temperature dependence of diffusion coefficients for Sample I

The diffusion coefficient of the type I relaxation results as:

$$D = D_0 e^{-E/kT} = 2.4 e^{-0.3eV/kT} (cm^2 s^{-1}) \qquad (6)$$

We also compared our measured diffusion coefficients, which were in the range of 3.5×10^{-6} – 7.5×10^{-6} $cm^2 s^{-1}$, with the already published results of Lyubomirsky [7], Jones [8] and Belas [1], showing a good correlation with the latter one, where $D \sim 3 \times 10^{-6}$-4×10^{-6} cm^2/s at 100°C was reported. The electro-diffusion measurements [1] of CdTe showed that the fast diffusing impurities/defects in p-type CdTe samples are donors, thus we assume analogous character of defects in our case. The nature of contaminating donors is unknown yet. Group I elements Li, Na, Cu, Ag, are mostly presumed [1]. Impurities may originate from the source 6N elements, quartz ampoule in which the crystal is grown and from ambient conditions together with the outside effects during the sample preparation and contacting procedure.

From the measurement of the hole relaxation, we could estimate the density of the donors, which is connected to the change of the hole concentration during the relaxation procedure. The estimated donor concentration for Sample I is $\sim 10^{13} cm^{-3}$ while the mobility had constant character during the relaxation, which reflects good crystal quality. For Sample II the estimated donor concentration is $\sim 10^{14} cm^{-3}$ while the mobility was slightly decreasing which can be connected to the non-homogeneity of the sample. The aforementioned concentration values are at the resolution limits of the glow discharged mass spectroscopy (GDMS). For the identification of elements responsible for reported phenomena the secondary ion mass spectroscopy (SIMS) measurements are planned.

CONCLUSIONS

The thermal stability of two p-type CdTe single crystals cut from different parts of as grown ingot was studied by conductivity and Hall-effect measurements. Step-like change of temperature in the interval 30-100°C was followed by a dwell, in which the relaxation of resistivity and Hall coefficient was stored. Whilst Sample I exhibited increasing/ decreasing resistivity after increasing/decreasing temperature step, an opposite behavior was identified at Sample II. Faster relaxation of Sample I allowed us to establish the activation energy of the process 0.3 eV. The relaxation effects were attributed to fast diffusing group I donors penetrating the material at the densities $\sim 10^{13} cm^{-3}$ in Sample I and $\sim 10^{14} cm^{-3}$ in Sample II.

ACKNOWLEDGEMENT

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