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Temperature dependent resistivity and Hall effect in proton irradiated CdS thin films

L. ION[a,*], V. GHENESCU[b], S. IFTIMIE[a], V. A. ANTOHE[a], A. RADU[a], M. GUGIU[c], G. VELISA[c], O. PORUMB[a], S. ANTOHE[a]
[a] *Faculty of Physics, University of Bucharest, 405 Atomistilor, P.O. Box MG-11, 077125, Magurele-Ilfov, Romania*
[b] *Institute of Space Sciences, 409 Atomistilor, P.O. Box MG-23, 077125, Magurele-Ilfov, Romania*
[c] *Horia Hulubei National Institute of Physics and Nuclear Engineering, 407 Atomistilor, P.O. Box MG-6, 077125, Magurele-Ilfov, Romania*

Cadmium sulphide finds extensive applications in a variety of optoelectronic devices. In particular, CdS thin films are suitable for use as windows in heterojunction solar cells that employ CdTe, Cu_2S or $CuInSe_2$ as an absorber. Such thin film based solar cells are well suited for use in space technology. For that specific application, it is important to know how ionizing radiations change their performances. We have investigated the effects of irradiation with high energy protons (3 MeV), at 10^{14} fluency, on electrical properties of polycrystalline CdS thin layers . The samples were prepared by thermal vacuum deposition from single source onto optical glass substrate. Temperature dependent electrical resistivity and Hall effect, before and after irradiation, were recorded from 300 K down to 4 K. The experimental results can be explained in the frame of a two-band model. Above 100 K electrical properties are controlled by a defect level of donor type, with an ionization energy of about 0.060eV. The possible origin of this defect is discussed.

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1. Introduction

The physical properties (such as its direct wide bandgap of 2.35 eV in the thermodynamically stable würtzite phase), as well as its good chemical and mechanical stability, recommend Cadmium Sulphide as a semiconductor well suited for electronic and optoelectronic applications, particularly in the thin film based solar cells technology. Such type of solar cells are of prime importance for use in space technology. CdS is widely used as a *n*-type window material in thin film CdS/CdTe solar cells, which are recognized as good candidates for low cost and producing efficient single-junction photovoltaic devices.

It is well known that the performance of the devices based on thin films strongly depends on optical and electrical transport properties of the films obtained under various experimental conditions. Electrical transport properties of the CdS thin films were investigated by many researchers [1-5], the influence of growth conditions, substrates and post-processing annealing being emphasized. However relatively little work was done on the influence of ionizing radiations on their physical properties [6,7]. Particularly, it is important to investigate the effect of proton irradiation, taking into account that the weight of protons in the cosmic rays is about 87%.

Here we approach the study of the effects of proton irradiation on the electrical transport properties of polycrystalline CdS layers. The temperature dependences of both electrical resistivity and Hall coefficient were analyzed, before and after irradiation with 3 MeV protons, at a fluence of 10^{14} cm^{-2}. The paper is organized as follows: details concerning the experimental procedures we have used are given in section 2. The results are discussed in section 3 and the main conclusions are summarized in the final section.

2. Experimental details

CdS thin films, 7 μm thick, were prepared by thermal vacuum evaporation of CdS powder onto a glass substrate. CdS powder (Aldrich) was sublimated at a pressure of 10^{-5} Torr from a quartz container, heated to 770 ºC, the substrate temperature being maintained at 270 ºC. To reduce the sputtering of the powder during the sublimation process, the evaporator was covered with a quartz-wool plug. To improve the structural and chemical homogeneity of the films, they were thermally treated in vacuum at 350 ºC for 15 minutes. The obtained CdS layers were subjected to irradiation with protons supplied by a Van de Graaff accelerator. The incident proton beam was directed perpendicularly to the surface of the samples. Irradiation was performed in an evacuated chamber, at ambient temperature, with 3 MeV protons to a fluence of 10^{14} protons/cm^2. The thermal effect during irradiation was negligible.

Electrical resistivity and Hall efect were recorded in van der Pauw configuration, by introducing the samples in a He closed cycle cryostat. During the measurements the pressure in cryostat was below 10^{-4} Torr. Electrical measurements were performed by using a Keithley 2400 source-meter and a Keithley 6517a electrometer, in the temperature range allowed by our experimental setup (4 – 300 K).

3. Results and discussion

The Arrhenius plot of the measured electrical resistivity as function of temperature is shown in Fig. 1. The experimental results suggest that there are two conduction mechanisms, namely Bloch-band conduction controlled by a single donor dominates in the high temperature range while impurity-band conduction dominates at low temperatures:

$$\rho^{-1}(T) = \rho_c^{-1}(T) + \rho_i^{-1}(T) \tag{1}$$

In equation (1) the first term $\rho_c^{-1}(T) = \sigma_c(T) = \sigma_{c0}(T)\exp\left(-\frac{E_d}{k_B T}\right)$ describes the (Bloch) band conduction in a non-degenerate semiconductor in a temperature range where the electrons are gradually recaptured by donors having the ionization energy E_d and the pre-exponential factor $\sigma_{c0}(T)$ has a weak temperature dependence due to the mobility of the free carriers; the second term $\rho_i^{-1}(T) = \sigma_i(T) = \sigma_{i0}\exp\left(-\frac{E_{ai}}{k_B T}\right)$ corresponds to impurity band conduction (hopping), characterized by a much smaller activation energy E_{ai}.

One can easily observe that proton irradiation in the above mentioned conditions does not affect significantly the $R(T)$ dependence at temperatures above 100 K where the Bloch band conduction mechanism dominates. However, significant changes can be seen in the low temperature range. The transition to impurity band conduction occurs at about 70 K before irradiation and at about 100 K after irradiation with protons. Moreover, at temperatures lower than the above mentioned limits the resistivity gets significantly smaller values after irradiation. This is consistent with the impurity band hopping, the resistivity depending exponentially on the density of the defect centers. It follows that the irradiation with protons increases the density of the main donors.

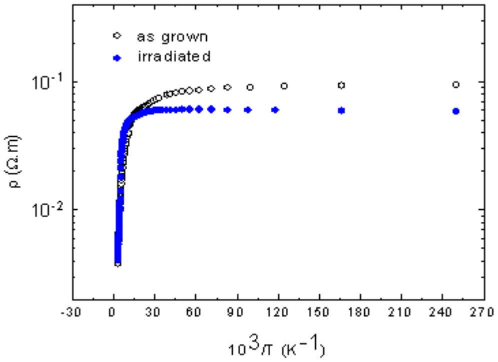

Fig. 1. Temperature dependence of the resistivity, before and after irradiation.

This conclusion is supported also by the temperature dependent Hall effect data (Fig. 2), where the transitions from high temperature band conduction mechanism to low temperature impurity band hopping can be clearly seen as peaks in $R_H(T)$ Arrhenius plots. $R_H = \frac{U_H d}{I_x B}$ is the Hall coefficient, U_H is the Hall voltage, I_x is the current trough the sample having the thickness d, B is the magnetic field, oriented perpendicularly to the surface of the film. The film exhibits a n-type conduction.

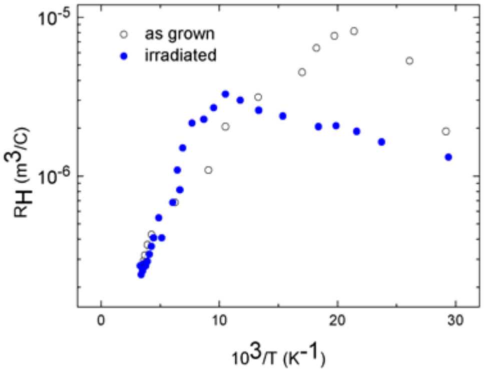

Fig. 2. Temperature dependence of the Hall constant, before and after irradiation, in Arrhenius plot.

These peaks can be explained in the frame of a two-band model. Thus, the contribution to the conductivity in eq. (1) from conduction-band (Bloch) electrons can be further expanded as:

$$\sigma_c(T) = e\,\mu_c(T)\,n_c(T) \tag{2}$$

while impurity-band electrons contributes with the term:

$$\sigma_i(T) = e\,\mu_i(T)\,n_i(T) \tag{3}$$

where $n_{c,i}$ and $\mu_{c,i}$ are the corresponding densities of carriers and mobilities of the two types of carriers, e being the absolute value of the electron charge.

Denoting the conduction-band Hall coefficient by $R_{Hc}(T) = \frac{r_{Hc}}{e n_c(T)}$, r_{Hc} being a coefficient with the magnitude of the order of unity related to the scattering mechanism of free electrons, and impurity-band Hall coefficient by $R_{Hi}(T)$, the following expression is obtained for the total Hall coefficient:

$$R_{Ht} = \frac{R_{Hc}\,\sigma_c^2 + R_{Hi}\,\sigma_i^2}{(\sigma_c + \sigma_i)^2} \tag{4}$$

If the impurity-band Hall mobility $\mu_{Hi}(T) = R_{Hi}\sigma_{Hi}$ is much smaller than its conduction-band counterpart $\mu_{Hc} = R_{Hc}\sigma_{Hc}$, and if the temperature is not too low, the first term in the numerator of eq. (4) dominates:

$$R_{Ht} \approx \frac{R_{Hc}\,\sigma_c^2}{(\sigma_c + \sigma_i)^2} \qquad (5)$$

By decreasing the temperature, the right hand side in the equation (5) will show a peak at temperatures where the conduction mechanism shifts from Bloch-band conduction to impurity-band conduction ($\sigma_c \approx \sigma_i$). At much higher temperatures than that corresponding to the peak, for a non-degenerate semiconductor, eq. (5) gives:

$$R_{Ht} \approx R_{Hc} \propto \exp\left(-\frac{E_d}{k_B T}\right) \qquad (6)$$

while at lower temperatures the following expression is obtained:

$$R_{Ht} \approx \frac{R_{Hc}\,\sigma_c^2}{\sigma_i^2} = \frac{e\,\mu_{Hc}\,\mu_c n(T)}{\sigma_i^2} \propto \exp\left(\frac{2\,E_{ai} - E_d}{k_B\,T}\right) \qquad (7)$$

where μ_c is the drift mobility of free carriers ($\mu_{Hc} = r_{Hc}\,\mu_c$).

In the high temperature range the activation energy of the Hall coefficient was 0.06 eV, similar with that found from the temperature dependence of the resistivity (0.062 eV), proving the validity of our model. The temperature dependence of the Hall mobility, before and after irradiation, in this temperature range is shown in Fig. 3. The mobility of the free carriers is slightly reduced after irradiation, due to the increased density of (charged) defects. We have to stress that previous investigations [8] have shown that the irradiation in the mentioned conditions mainly introduces point-like defects; no extensive damage was observed.

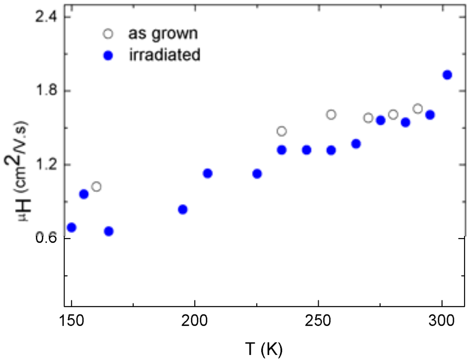

Fig. 3. Temperature dependence of the Hall mobility before and after irradiation.

In order to get a more detailed picture of the proton irradiation damage in our film, the software package SRIM-2008 [9] was used in full collision cascade mode.

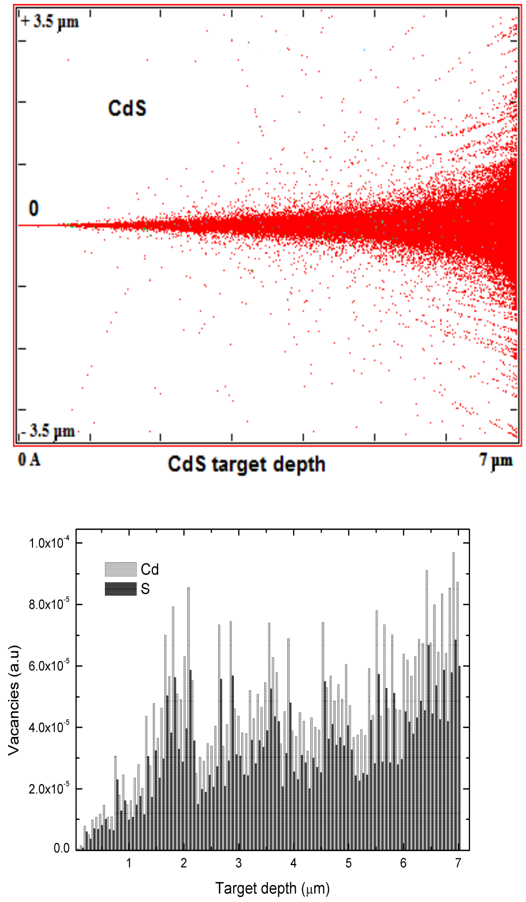

Fig. 4. Monte Carlo simutation of 3 MeV proton scattering distribution and Cd and S vacancies distribution in CdS thin layer.

Fig. 4 shows the result of a Monte-Carlo simulation of proton spatial scattering distribution and the Cd and S vacancies distribution in CdS thin film. At this proton energy most of the protons are transmitted. The scattering events occur in a significant fraction at the interface with the glass substrate. Except for a region near the surface of the film, 1.5 µm thick, Cd and S vacancies are produced relatively uniformly in CdS layer.

3. Conclusions

An investigation on the effects of 3 MeV proton irradiation on electrical properties of CdS polycrystalline thin films grown by vacuum deposition was performed. The behavior of the Hall effect and the resistivity curves over the entire temperature range can be satisfactorily accounted for on the basis of a two-band model.

Two types of carriers in different energy bands and with different mobilities contribute to electrical conduction of the film. At high temperatures electrical properties are controlled by a single donor center, partially compensated, having an ionization energy of about 0.06 eV. We infer that this defect center corresponds to sulfur vacancies [10] or to more complex aggregates of them. It is possible that these defects have been generated during the film growth or the thermal treatment. Moreover, proton irradiation increases their density, as proved by the important changes observed in both resistivity and Hall coefficient in the low temperature range. This conclusion is also supported by a Monte Carlo simulation which shows that irradiation mainly introduces point-like defects (vacancies and interstitials or their more complex aggregates). The much less important effect in the high temperature range, where the contribution of conduction band electrons to the conductivity dominates, is to be associated with the introduction of Cd vacancies which act as acceptors (electron traps). The calculated energy levels corresponding to singly occupied V_{Cd}^{-} centers and doubly occupied V_{Cd}^{2-} centers are at 0.33 eV, respectively 0.51 eV above the top of the valence band [11]. They compensate the donor centers, and so the density of free carriers is not changed significantly.

Acknowledgments

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*Corresponding author: lucian@solid.fizica.unibuc.ro