

## STRUCTURE AND ELECTRICAL PROPERTIES OF ELECTRON IRRADIATED CdSe THIN FILMS

L. Ion<sup>a\*</sup>, S. Antohe<sup>a</sup>, M. Popescu<sup>b</sup>, F. Scarlat<sup>c</sup>, F. Sava<sup>b</sup>, F. Ionescu<sup>b</sup>

<sup>a</sup>University of Bucharest, Faculty of Physics, 077125 Măgurele-Ilfov, POB MG-11, Romania

<sup>b</sup>INCDFM Bucharest, 077125 Măgurele-Ilfov, Romania

<sup>c</sup> Valachia University, Târgoviște, Romania

Structural and electrical properties of polycrystalline CdSe thin films irradiated with high-energy electrons are analyzed. The samples were prepared by vacuum deposition onto optical glass substrate. Their structure and the temperature dependence of the electrical resistance were determined, both before and after irradiation with 6 MeV electrons and fluencies up to  $10^{16}$  electrons/cm<sup>2</sup>. There were no measurable changes in the crystalline structure of the films after irradiation. Electrical properties are controlled by a defect level of donor type, possibly a selenium vacancy, with two charge states having ionization energies of about 0.40 eV, respectively 0.22 eV. Irradiation increases significantly the concentration of those defects.

(Received February 28, 2003; accepted after revision January 28, 2004)

*Keywords:* Polycrystalline thin films, CdSe, Electron irradiation

### 1. Introduction

The optical and electrical properties, as well as its good chemical and mechanical stability, recommends Cadmium Selenide (CdSe) as a semiconductor well suited for optoelectronic applications, such as photo-detection or solar energy conversion. It is a well known fact that the quality of the devices based on CdSe thin films strongly depends on the structural and electronic properties of the films obtained under various experimental conditions. Many reports have been published on the preparation and electrical properties of the vacuum-deposited films of A<sup>II</sup>- B<sup>VI</sup> compounds [1-6]. But, despite this considerable amount of work, only a few studies on the influence of the ionizing radiations on their electrical properties have been performed [7-11]. In this paper we present the results of a structural and electrical investigation on polycrystalline thin films of CdSe subjected to high-energy electron irradiation. The films were prepared by thermal vacuum-evaporation onto glass substrates.

### 2. Experimental procedures

CdSe thin films, 40 μm thick, were prepared by thermal vacuum evaporation from a single source onto an optical glass substrate. The pressure in the evaporation cell was kept below  $2 \times 10^{-5}$  Torr during the deposition of the films. The evaporator consisted of a quartz container heated to 750 °C, the substrate being maintained at 220 °C during the deposition. To improve the structural and chemical homogeneity of the films, they were subsequently thermally treated in vacuum at 300°C, for 10 min. Then four Al contacts were evaporated on CdSe. The contacts, 1 mm×1 mm in surface, 0.3 μm thick and separated by 1 mm, were placed in line.

The obtained structures were subjected to irradiation with electrons supplied by a betatron. The samples were irradiated at room temperature with 6 MeV electrons to a fluence of

---

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

$10^{15}$  electrons/cm<sup>2</sup>, irradiation direction being perpendicular to the surface of the samples and the thermal effect during irradiation was negligible.

The structure of the samples was investigated, before and after irradiation, with a  $\theta$ -2 $\theta$  X-ray diffractometer, using Cu-K $\alpha$  ( $\lambda=1.54178$  Å) line. Line profiles were recorded in a step-scanning regime with  $\Delta(2\theta)=0.05^\circ$ . The temperature dependence of the electrical resistance and I-V characteristics were recorded by introducing the samples in a He closed cycle cryostat and contacting the probes with soft Ag wire. During the measurements the pressure in cryostat was below  $10^{-4}$  Torr. Electrical properties were measured with a Keithley 2400 source-meter, in the temperature range allowed by our experimental setup.

### 3. Experimental results

#### A. Structure

Fig. 1 shows the experimental XRD pattern of two samples. It indicates the presence of wurtzite-type (hcp) structure, which is known to be the stable one for this material. The films are oriented with (001) crystalline direction perpendicular to their surface. The position of the peaks yields hcp lattice constants of  $4.296\text{\AA}$  ( $a_h$ ) and  $7.030\text{\AA}$  ( $c_h$ ). While  $a_h$  is consistent with the reported bulk value,  $c_h$  is somewhat larger.

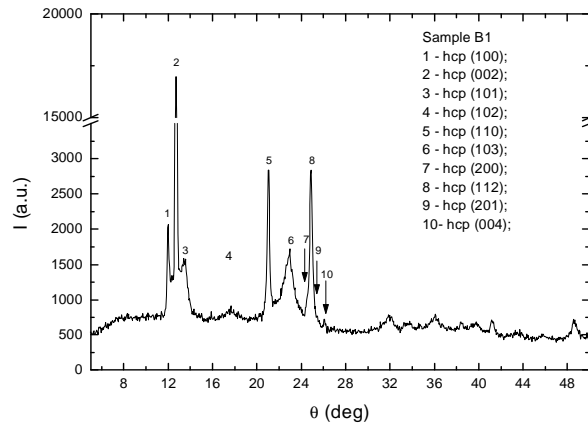


Fig. 1. Experimental X-ray diffraction pattern of a CdSe thin film sample.

A simple inspection of the diffraction pattern shows that both broadened lines and sharp reflections are present. An explanation for this [12] has been given as due to faulting. In the case of crystals made up of close-packed layers of atoms, stacking faults (mistakes in the normal hexagonal or cubic packing order) may easily occur. The energy of producing such defects is very low. For reflections of the type  $(hk0)$ ,  $(00l)$  and  $(hkl)$  with  $h=k=3n$ , there is no change in structure factor on crossing the fault, therefore no broadening is observed. In contrast, for  $(hkl)$  reflections with  $h-k=3n\pm1$ , the structure factor changes significantly at each fault, which results in broadening the line. The amount of broadening depends on the number of stacking faults.

A measure of the coherence length of the periodic structural pattern corresponding to a particular peak can be obtained from its width through the well-known Scherrer formula:

$$D_{eff} = \frac{0.9\lambda}{\delta \cos \theta_0}, \quad (1)$$

where  $D_{eff}$  is the coherence length,  $\lambda$  is the X-ray wavelength,  $\theta_0$  is the angle where the peak occurs and  $\delta$  is its full width at half-maximum.  $D_{eff}$  values, calculated for three samples from (002) peak, are indicated in Table 1.

Table 1. Coherence length, as determined from (002) peak.

Sample	$D_{eff}$ (Å)
B1	1072
B2	1352
B3	1587

Within the limits of experimental resolution, no change in diffraction pattern aspect or in line broadening was observed following electron irradiation at fluences up to  $10^{16}$  electrons/cm<sup>2</sup> (Fig. 2). Therefore there are no major changes in the crystalline structure of the films, as a result of electron irradiation at energy and fluences indicated above. It may be concluded that at most point-like defects (vacancies, interstitials or their association in some more complex defects) do occur in the structure of the films.

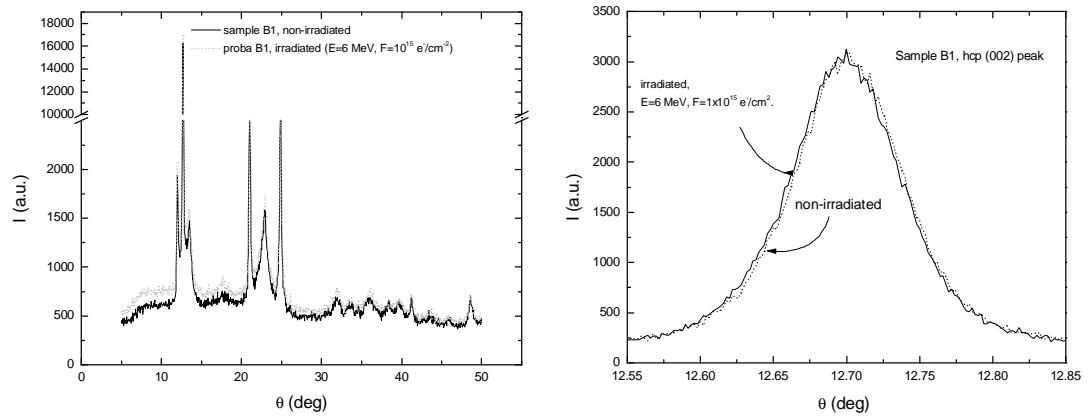


Fig. 2. X-ray diffraction pattern and hcp (002) peak for sample B1, before and after irradiation.

## B. Electrical properties

The temperature dependence of the electrical resistance, recorded for one sample, before and after irradiation, is shown in Fig. 3. All the studied samples are of n-type, as confirmed by Hall effect data (Fig. 4). Irradiation parameters are also indicated in legend.

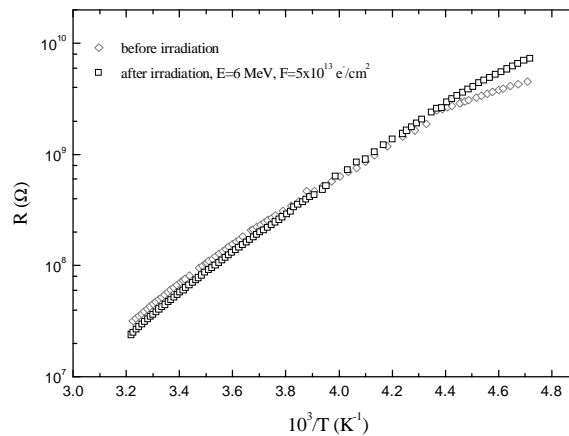


Fig. 3. Temperature dependence of electrical resistance, before and after irradiation.

This dependence is of activated type:

$$R(T) = R_0 \exp\left(\frac{E_{ac}}{k_B T}\right) \quad (2)$$

but has different activation energies in the upper and lower region of the investigated temperature range. The values of the parameters entering eq. (2), as obtained by numerical fit, are indicated in Table 2.

Table 2. Parameters describing the temperature dependence of the electrical resistance of CdSe thin films (eq.2).  $R_{10}$  and  $E_{a1}$  are the values corresponding to higher temperature range, while  $R_{20}$  and  $E_{a2}$  correspond to lower temperatures.

Sample	$R_{10}$ ( $\Omega$ )	$E_{a1}$ (eV)	$R_{20}$ ( $\Omega$ )	$E_{a2}$ (eV)	Comments
B3	18.62	0.38	$2.57 \times 10^6$	0.18	- non-irradiated sample;
B3	53.11	0.36	$3.51 \times 10^5$	0.21	- irradiated, 6 MeV electrons, $5 \times 10^{13} \text{ e}^-/\text{cm}^2$ ;

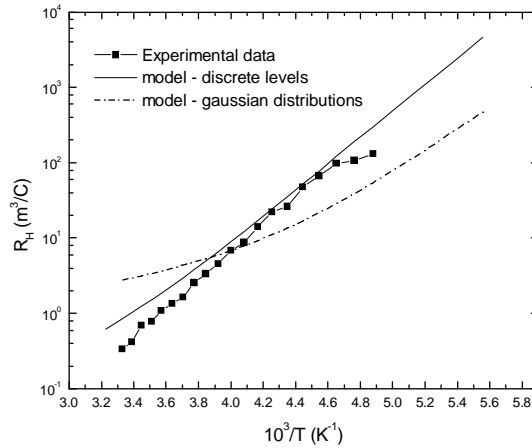


Fig. 4. Temperature dependence of the Hall constant (sample B3). Points represent experimental data, while lines represent model results as described in text.

At room temperature and down to 250 K, the experimental results suggest a band conduction mechanism, controlled essentially by a deep donor level ( $E_I$ ) located at about 0.40 eV below the bottom level of the conduction band. This is also supported by the Hall effect data (Fig. 4). In this region the temperature dependence of the electrical resistance is entirely due to the rapid decrease in the concentration of the free carriers (electrons), that are gradually recaptured by the donor levels they originate from. After irradiation a higher value of  $R_{10}$  is recorded, so the mobility of free carriers diminishes, probably as a result of an increased concentration of ionized donors.

It is worth pointing out that in the low temperature region the pre-exponential coefficient  $R_{20}$  drops by almost an order of magnitude after irradiation (see Table 2). Also a significant decrease of the activation energy of the Hall constant  $R_H$  is observed. This suggests a change in the conduction mechanism at temperatures below 230 K. The experimental results may be explained by connecting the electrical conduction mechanism in this temperature range with the motion of electrons over some other (donor) states ( $E_2$ ), located at about 0.18 eV above the  $E_I$  level where the Fermi level is pinned (Fig. 5).

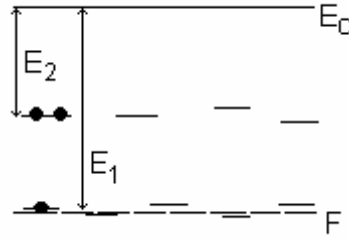


Fig. 5. Energy levels corresponding to a donor defect with two ionization states.

It was suggested [2,11] that  $E_1$  level could be related to a defect implying selenium vacancy. But such a defect can exist in two charge states, simply and doubly ionized. We believe that  $E_1$  and  $E_2$  levels correspond to two charge states of a defect involving a selenium vacancy,  $V_{Se}^+$  and  $V_{Se}^0$  respectively:



Due to compensation, only the second of the above processes generates free electrons, the Fermi level is pinned at  $E_1$  below conduction band and the band conductivity depends on temperature according to

$\sigma_b \propto e^{-\frac{E_1}{k_B T}}$ . That is the situation observed from room temperature down to 250 K, the activation energy of the electrical resistance being  $E_{a1}=E_1$ . At lower temperatures the number of free electrons is exponentially small, and a hopping mechanism comes into first place. Localized electrons can hop from a  $V_{Se}^+$  state to a  $V_{Se}^{++}$  state or from a  $V_{Se}^0$  to  $V_{Se}^+$ , etc. The former situation corresponds to hopping from an occupied  $E_1$  state to an empty one, requires partial compensation, results in small activation energy of the conductivity and should be the most important process at very low temperature. The latter situation corresponds to hopping between  $E_2$  (neutral) states; the number of hopping electrons is exponentially small  $\left( \propto e^{-\frac{E_1-E_2}{k_B T}} \right)$ , but their mobility is higher due to a larger

localization radius of the  $E_2$  state. For that reason the above mentioned mechanism could become dominant in some finite temperature range. It results in an activation energy of the conductivity  $E_{a2}=E_1-E_2$ , and also can explain the experimentally observed decrease of the pre-exponential factor  $R_{20}$ . Electron irradiation generates new such defects, the overlap of the localized wave functions becomes more pronounced and hence an exponentially smaller  $R_{20}$  value results.

For testing the above assumption (donor defects with two ionization states), a model for the temperature dependence of the Hall constant for a CdSe crystal with a donor defect having two ionization states and a partially compensating acceptor defect was also developed, the results being presented in Fig. 4. For the sake of simplicity, the bottom level of the conduction band was chosen as energetic reference ( $E_c=0$ , Fig. 5). At some given temperature donor defects can exist in equilibrium in neutral (concentration  $N_d^0$ ), singly ( $N_d^+$ ) or doubly ionized ( $N_d^{++}$ ) states. Acceptor levels are fully occupied, due to compensation. The equation expressing electrical neutrality of the crystal reads:

$$n + N_a = N_d^+ + 2N_d^{++}, \quad (4)$$

where  $N_a$  is acceptor concentration, and:

$$N_d = N_d^0 + N_d^+ + N_d^{++}. \quad (5)$$

Equations relating the quantities appearing in eq. (5), are given by standard Fermi statistics for a doped semiconductor:

$$\frac{N_d^0}{N_d^+} = \frac{g_0}{g_+} \exp\left(\frac{F - E_2}{k_B T}\right), \quad \frac{N_d^+}{N_d^{++}} = \frac{g_+}{g_{++}} \exp\left(\frac{F - E_1}{k_B T}\right), \quad (6)$$

where  $g$ 's are the degeneracy factors of the corresponding states ( $g_0 = g_{++} = 1$ ,  $g_+ = 2$  accounting for the two spin states),  $E_1$  and  $E_2$  are ionization energies as introduced in eq. (3) (see also fig. 5). Using eqs.

(5)-(6) and taking into account that  $n = N_c \exp\left(\frac{F}{k_B T}\right)$ , eq. (4) becomes:

$$n + N_a = N_d \frac{1 + \frac{N_c}{n} \exp\left(\frac{E_2}{k_B T}\right)}{1 + \frac{n}{2N_c} \exp\left(-\frac{E_1}{k_B T}\right) + \frac{N_c}{2n} \exp\left(\frac{E_2}{k_B T}\right)}. \quad (7)$$

The above equation was numerically solved, with  $N_c = 2.23 T^{3/2} \times 10^{14} \text{ cm}^{-3}$ , typical for CdSe,  $E_1 = 0.4 \text{ eV}$ ,  $E_2 = 0.22 \text{ eV}$  and a compensation factor  $k = N_a/N_d = 0.1$ . The results are indicated as solid line in Fig. 4. The dashed line represents the results obtained as indicated above, but for a gaussian-like continuous distribution of donor levels, centered at  $E_1$  and  $E_2$  and 0.1 eV wide. It is obvious that the discrete levels solution is closer to experimental data.

#### 4. Conclusions

Structure and electrical properties of CdSe thin films irradiated with high-energy electrons were investigated. The films contain wurtzite-type CdSe, (001) preferentially oriented in the growth direction, with some amount of stacking faults. The coherence length as determined from (002) diffraction line broadening, was about 1000 Å for all analyzed samples. No changes in the general aspect of the diffraction pattern, or in line broadening were observed after irradiation, within the limits of experimental resolution. It may be concluded that this type of irradiation, in analyzed conditions, produces only some type of point-like defects in the crystalline structure of the films.

Electrical properties of the films can be explained by assuming that they are controlled by a deep donor defect, possibly selenium vacancy, having two ionization states, with ionization energies of 0.40 eV, respectively 0.22 eV (eq. 3). In the temperature range extending from room temperature down to about 250 K, the band conduction mechanism is dominant, while below 230 K electrical conduction is due to electrons hopping over singly filled donors. After irradiation the concentration of these donors increases; this can explain the observed behavior of resistance pre-exponential factors  $R_{10}$  and  $R_{20}$ . A model was developed for calculating the temperature dependence of the Hall constant for a semiconductor crystal with a defect existing in two ionization states. Its results agree reasonably well with experimental data.

A shift of activation energies of the electrical resistance was also observed after irradiation with high energy electrons. Such an irradiation generates new defects of vacancy and/or interstitials type [13]. Due to a better overlapping of the localized wave functions and also due to Coulomb interactions, the defect levels are scattered in energy, resulting a wider impurity band. The texture of the films can also play a role: electron irradiation can affect the energetic potentials at grain boundaries, determining a shift of the mobility edge in the conduction band. These two effects could be responsible for the observed shifts of activations energies.

### References

- [1] L. L. Kazmerski, W. B. Berry, C. W. Allen, J. Appl. Phys. **43**(8), 3515-3526, (1972).
- [2] Kazuo-Shimizu, Japanese Journal of Applied Physics **4**(9), 627, (1965).
- [3] B. B. Ismail, R. D. Gould, Phys. Stat. Sol. (a), **115**, 237, (1989).
- [4] R. D. Gould, B. B. Ismail, Int. J. Electron. **69**, 19-24, (1990).
- [5] A. M. Andriesh, V. I. Verlan, L. A. Malahova, J. Optoelectron. Adv. Mater **5**(4), 817 (2003).
- [6] M. Lisca, E. Pentia, G. Sarau, L. Pintilie, I. Pintilie, T. Botila, J. Optoelectron. Adv. Mater. **5**(4), 849 (2003).
- [7] B. A. Kulp, Phys. Rev. **125**, 1865, (1962).
- [8] H. Ohyama, K. Hayama, Phys. Stat. Sol. (a) **142**, K.117, (1994).
- [9] I. Spănulescu, I. Secareanu, N. Băltăteanu, I. Z. Abdi, T. Khalass, Thin Solid Films **143**, 1-6, (1986).
- [10] S. Antohe, L. Ion, V. Ruxandra, J. Appl. Phys. **90**(12), 5928 (2001).
- [11] S. Antohe, L. Ion, V. A. Antohe, J. Optoelectron. Adv. Mater. **5**(4), 801 (2003).
- [12] E. F. Kaelble (ed.), "Handbook of X-Rays", chapt. 17, McGraw-Hill, New York, USA, 1967.
- [13] J. W. Corbett, "Solid State Physics", vol. 7 suppl. ("Electron Radiation Damage in Semiconductors and Metals"), Academic Press, New York, 1966.