Electronic transport and photoconductivity of polycrystalline CdSe thin films

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In this paper we have studied the electrical properties and photoconductivity of CdSe thin films, prepared by vacuum evaporation using the quasi-closed volume technique. It was found that the films were polycrystalline with a hexagonal (würtzite) structure and the crystallites are highly oriented with the (002) planes paralel to substrate. The film surface was investigated by means of SEM. The temperature dependence of electrical conductivity and Seebeck coefficient was studied. The films have n-type conduction. The spectral characteristics of photoconductivity were studied at 78 K and 300 K in the wavelength range 300–1100 nm. The bandgap energy (1.53–1.63 eV) calculated by using the Moss rule is smaller than those determined from absorption spectra. For the diffusion length, determined form absorption spectra and spectral dependence of photoconductivity, values between 0.22 and 0.29 μm were found.

1. Introduction

Cadmium selenide (CdSe) thin films have been constantly investigated during recent years for both fundamental and practical importance [1-3]. Its interesting properties makes the material suitable for many potential applications in a variety of solid state devices such as solar cells, high-efficiency thin film transistors, light-emitting diode, electron-beam pumped lasers and electroluminescent devices, etc [3-7].

Among other preparation techniques thermal evaporation under vacuum is a very convenient method for obtaining uniform films under different deposition parameters.

In previous papers [8-10] we have studied optical properties of polycrystalline CdSe thin films using the quasi-closed volume technique [11]. In this paper electrical properties and photoconductivity of polycrystalline CdSe thin films are investigated.

2. Experimental

CdSe thin films onto glass substrates were prepared by thermal evaporation under vacuum of CdSe polycrystalline powder (99,999% purity), using the quasi-closed volume technique [11]. CdSe thin films were prepared in various deposition conditions: the substrate temperature, T_s, was varied between 300 K and 500 K and the temperature of evaporation source, T_{ev}, between 900 and 1100 K.

The structure of the films was studied by X-ray diffraction (XRD) using CoK_α radiation. The surface morphology of the films was investigated by means of scanning electron microscopy (SEM).

The thickness of the films (d = 0.20-1.80 μm) was measured using an interferometric method [12].

The temperature dependence of electrical conductivity, σ, was studied using surface type cells with indium films as electrical ohmic contacts.

The electrical resistance of the film and its temperature dependence were measured using a model 6517 Keythley electrometer.

The Seebeck coefficient was measured using the sonde method [13]. The temperature difference between sondes was of 10 - 15 K. The Seebeck voltage was determined by a standard potentiometric method using a Keithley M2170 multimeter.

The absorption coefficient, α, was calculated using the formula [14,15]

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2}{T} \right] \qquad (1)$$

where d represents the film thickness and R and T are the reflection and transmission coefficients. Transmission and reflection spectra (in the spectral range 300-1400 nm) were recorded using a PMQII type (C. Zeiss, Jena) spectrophotometer and an STEAG ETA-OPTIK spectrometer.

The photoconductivity spectra were recorded using a spectrometric arrangement based on a monochromator equipped with diffraction gratings (1200 nm^{-1} and 600 nm^{-1}). The experimental arrangement is described in detail in [15-18].

3. Results and discussion

3.1 The structure analysis of the films

The XRD patterns for CdSe films indicate that the samples are polycrystalline and have a würtzite (hexagonal) structure. The crystallites are preferentially

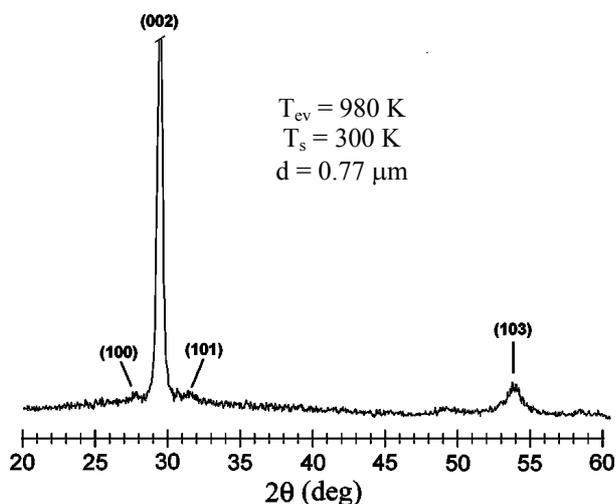oriented with the (002) plane parallel to the substrate, as shown on Fig. 1.

Fig. 1. Typical XRD pattern for CdSe thin films.

The method used for sample preparation takes into account the complete dissociation of the compound into Cd and Se_2 molecules during the evaporation process and their recombination on the substrate to form CdSe films. An incomplete recombination of the components on the substrate may lead to non-stoichiometric films [20]. No other phase except würtzite CdSe was identified in the XRD patterns. The sharp absorption edge (corresponding to the forbidden energy gap) observed for our CdSe films [8,9] might indicate that the films have a stoichiometric composition [20].

The average size of the crystallites (between 20 and 100 nm) was determined by means of XRD and SEM images (Fig. 2). It was found that the crystallite size increases with increasing film thickness, substrate temperature during deposition and the temperature of the evaporation source. A heat treatment after film deposition also determines an increase of the crystallite size [8].
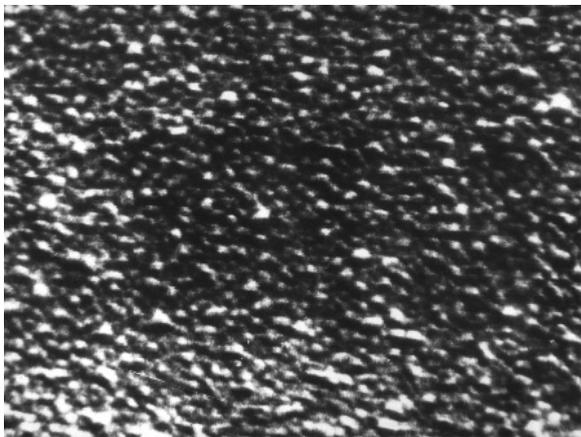

Fig. 2. SEM image (21000x) showing the polycrystalline structure of a CdSe thin film (T_{ev}=900 K, T_s=300 K, d=0.30 μm).

3.2 Electrical properties of the films

It was experimentally established [21,22] that for a great number of semiconductor materials in thin films, the stable structure of the films can be obtained if (after deposition) they are subjected to a heat treatment.

We studied the temperature dependence of the electrical conductivity for CdSe thin films during this heat-treatment, consisting of 2–3 heating/cooling cycles within the temperature range 300 – 500(or 700) K.

The typical shape of ln σ = f ($10^3/T$) curves during heat treatment are presented in Figs. 3 and 4.
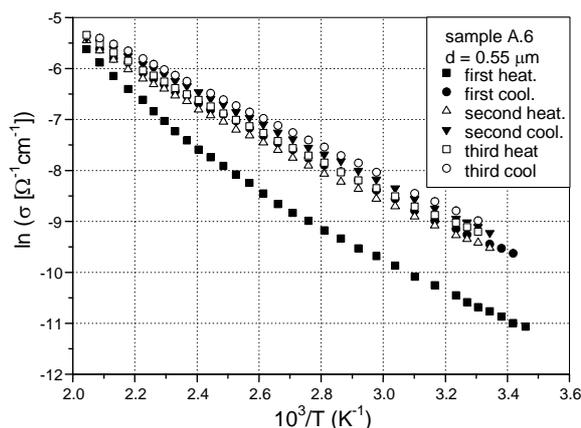

Fig. 3. Temperature dependence of electrical conductivity for a CdSe film during the heat treatment between 300 and 500 K (T_{ev}=900 K, T_s=300 K).

The electrical conductivity of as deposited CdSe films was significantly higher than the electrical conductivity of the intrinsic material, which is about 10^{-12} $\Omega^{-1}cm^{-1}$.

For all studied samples the electrical conductivity increases after the heat treatment. It is well known that in polycrystalline thin films the transport phenomena are strongly influenced by crystallite size and the characteristics of grain boundaries [3,12,23]. The increase of the electrical conductivity after the heat treatment, σ_T, can be explained by the increase of the crystallite size (which is observed for our samples) and probably by the reduction of the width of barrier layers at the grain boundaries.

From the point of view of electrical conductivities after deposition the investigated films show two distinct behaviours. If the temperature of the evaporation source is below 940 K the resulting films have smaller conductivities while for temperatures of the evaporation source above 940 K the conductivity of the films is higher.

For the samples with smaller conductivities (Fig. 3) on the first stage of the first heating the ln σ = f ($10^3/T$) dependence is linear. The thermal activation energy of electrical conductivity, E_{a0}, calculated from the relation [24]

$$\sigma = \sigma_0 \, exp\left(- E_a /kT\right) \qquad (2)$$

(where E_a is the activation energy of electrical conduction, k is Boltzmann's constant and T is the temperature) is about 0.20-0.27 eV. After the first cooling the electrical

conductivity is higher than its initial value, this process being irreversible. After 2-3 heating and cooling processes when the temperature dependence of electrical conductivity became reversible the $\ln \sigma = f(10^3/T)$ dependence is linear on the entire temperature range under study (200 ^{o}C). The corresponding activation energy, E_{a1}, is approximately the same with E_{a0}. This means that the structural modifications that took place in the course of the heat treatment have a minor influence on the mechanism of electrical conduction.
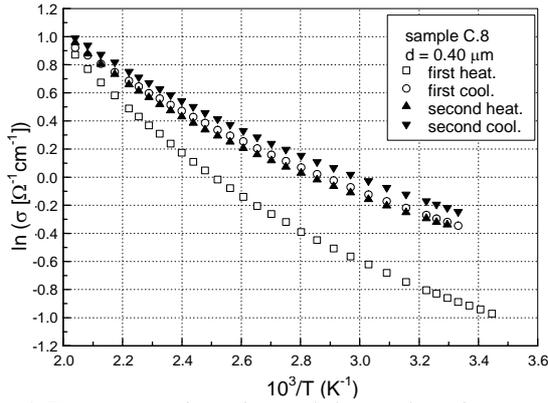

Fig. 4. Temperature dependence of electrical conductivity for a CdSe film during the heat treatment between 300 and 500 K (T_{ev}=980 K, T_s=300 K).

For the samples with higher conductivities (Fig. 4) on the first stage of the first heating the $\ln \sigma = f(10^3/T)$ dependence is also linear but the corresponding activation energy, E_{a0}, is smaller (about 0.04 – 0.10 eV). After the heat treatment this dependence shows two linear parts, corresponding to two different activation energies, E_{a1} and E_{a2}. In the smaller temperature range the activation energy E_{a1} is about 0.03 – 0.07 eV and in the higher temperature range the activation energy E_{a2} is about 0.10 – 0.12 eV. The transition temperature between this two linear parts is $T_0 = 382 \div 555$ K.

For the samples with smaller conductivities a heat treatment performed at 700 K makes the electrical conductivity to increase with several orders of magnitude so that the electrical behavior of this heat-treated samples became the same as for those with higher conductivities (Fig. 5)
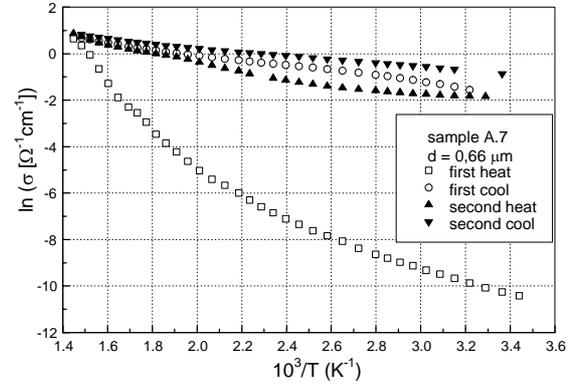

Fig. 5. Temperature dependence of electrical conductivity for a CdSe film during the heat treatment between 300 and 700 K (T_{ev}=900 K, T_s=300 K).

Some results are presented in Table 1.

The sign of the Seebeck coefficient was negative for all investigated samples, indicating that the electrons are the majority charge carriers and the studied samples have n-type conduction. The Seebeck coefficient was found to increase with increasing temperature.

From $\alpha = f(10^3/T)$ dependence, we found that Fermi level position is about 0.014 eV under the bottom of the conduction band.

In undoped CdSe n-type conduction is determined by the energy levels introduced in the forbidden gap by the native defects, interstitial Cd and Se vacancies and also by the complexes of these defects [6]. The increase of the electrical conductivity of CdSe films when the deposition rate increases (the evaporation source temperature increases) is due probably to an increase of the Se vacancies concentration

Table 1. Characteristic parameters of some investigated samples.

sample	T_{ev} (K)	ΔT (K)	d (μm)	σ (Ω^{-1}cm^{-1})	σ_T (Ω^{-1}cm^{-1})	E_{a0} (eV)	E_{a1} (eV)	E_{a2} (eV)	T_0 (K)
A.5	900	300-500	0.60	$2.3\ 10^{-5}$	$6.6\ 10^{-5}$	0.263	0.256	–	–
A.6	900	300-500	0.55	$1.6\ 10^{-5}$	$7.7\ 10^{-5}$	0.261	0.255	–	–
A.7	900	300-700	0.66	$3.0\ 10^{-5}$	0.4	0.268	0.067	0.115	555
B.3	940	300-500	1.10	0.2	0.4	0.043	0.041	0.050	382
B.4	1020	300-500	0.72	1.7	9.8	0.077	0.023	0.069	400
B.6	940	300-500	0.61	0.9	5.6	0.118	0.028	0.087	400
C.8	980	300-500	0.40	0.5	1.3	0.076	0.068	0.108	396
C.9	980	300-500	0.32	0.4	0.7	0.082	0.072	0.112	387

3.3 Photoconductivity spectra

The photoconductivity spectra were measured at 78 and 300 K. In Fig. 6 the typical normalized photoconductivity spectra are presented. The maximum of the photoconductivity shifts towards longer wavelengths with increasing temperature.

The values of the bandgap energy at 300 K (1.53 – 1.63 eV) calculated by using the Moss rule was smaller than those estimated from absorption spectra. From the spectral dependence of absorption coefficient a direct optical bandgap of 1.65 – 1.75 eV for the investigated CdSe thin films [8,9] was found. At 78 K the bandgap energy was about 1.73 –1.82 eV (Table 2).

For the temperature dependence of bandgap energy a simple linear relation was used. For the investigated samples the coefficient of this temperature dependence was found to be $3– 8 \times 10^{-4}$ eVK^{-1}.

We suppose that the slower decrease in photoconductivity in the wavelength domain 400-700 nm is due to trapping processes [6,18,23]. The shape of photoconductivity spectra at 300 K in the domain 300-500 nm shows that surface recombination velocity is small [17].
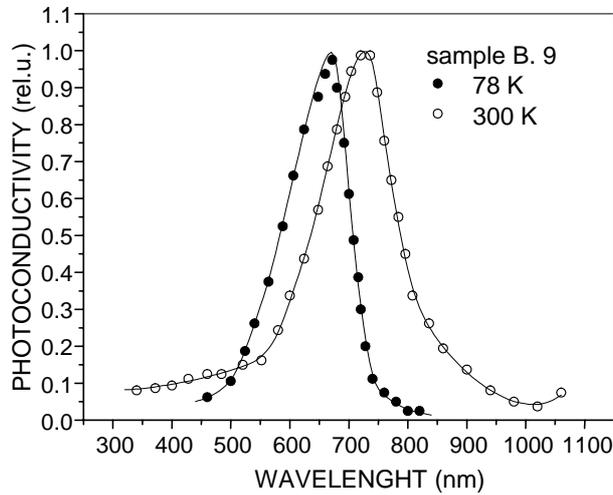

Fig. 6. Spectral dependence of photoconductivity for a CdSe film ($T_{ev}=900$ K, $T_s=300$ K, d =0.96 μm).

The excess carrier concentration can be found by solving the general equation of photoconductivity. The photoconductivity is proportional with the excess carrier concentration profile, which for a thin film can be calculated from the following equation [16,18]

$$\overline{\Delta n} = \frac{g_0\tau}{\alpha(1-\alpha^2 L_D^2)}\left[1-e^{-\alpha d} - \frac{\alpha s\tau\left(1+e^{-\alpha d}\right)+\alpha^2 L_D^2\left(1-e^{-\alpha d}\right)}{1+\frac{sL_D}{D}cth\frac{d}{2L_D}}\right] \quad (3)$$

where g_0 is the optical generation rate at the front surface of the film, τ is the recombination time, L_D is the ambipolar diffusion length, D is the ambipolar diffusion coefficient, α is the absorption coefficient, d is the thickness of the film and s is the surface recombination rate.

The wavelength dependence of absorption coefficient practically determines the spectral dependence of photoconductivity.

At low wavelengths, below the absorption edge, the values of the absorption coefficient are very high. If $\alpha d > 1$ şi $d/2L_D \gg 1$ then the relation (3) becomes

$$\overline{\Delta n(\alpha)} = \frac{\eta J_0(1-R)}{h\nu}\frac{1+\frac{s}{D}\frac{1}{\alpha}}{1+\frac{sL_D}{D}} \quad (4)$$

where η is the quantum efficiency, J_0 is the photon incident flux, R is the reflection coefficient of the front surface of the sample and $h\nu$ is the photon energy.
When $\alpha \to \infty$ one obtaines [3,5]

$$\overline{\Delta n(\infty)} = \frac{\eta J_0(1-R)}{h\nu}\frac{1}{1+\frac{sL_D}{D}} \quad (5)$$

If the photon flux $J_0/h\nu$ is constant and the wavelength dependence of the reflection coefficient can be neglected, the left term in relation (4) is a constant. As a result, in this spectral range, the photoconductivity should also be a constant. This type of behaviour can be observed in Fig. 6.

In the spectral range where relation (5) stands the variable

$$\frac{\overline{\Delta n(\infty)}}{\overline{\Delta n(\alpha)}-\overline{\Delta n(\infty)}}=\frac{\overline{\Delta\sigma(\infty)}}{\overline{\Delta\sigma(\alpha)}-\overline{\Delta\sigma(\infty)}}=\frac{D}{sL_D}\left(1+\alpha L_D\right). \quad (6)$$

linearly depends on the absorption coefficient.

From this linear dependence (Fig. 7) the diffusion length can be obtained. The intercept of the abscissa is

$$\alpha = -1/L_D \quad (7)$$

and in this way one can calculate the diffusion length. If the diffusion coefficient is known, from the intercept of the ordinate line the surface recombinate rate can also be determined.
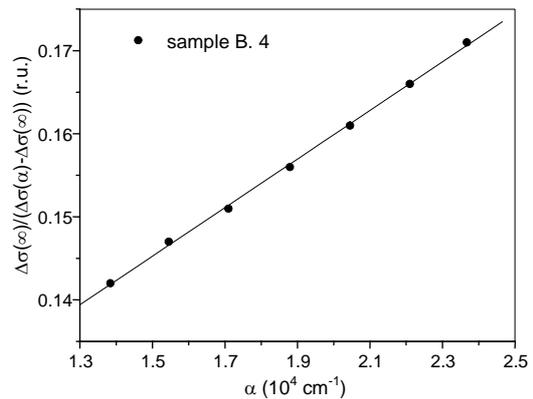

Fig. 7. Graphical calculation of the diffusion length.

For the diffusion length, determined form absorption spectra and photoconductivity spectra, values between 0.22 and 0.29 μm were found. For an n-type semiconductor the ambipolar diffusion length can be aproximated with the diffusion length of the holes, which are the minority charge carriers.

Table 2. Some characteristic parameters calculated from the photoconductivity spectra.

sample	d (μm)	maximum		ΔE (eV)		ΔE (0) (eV)	a (10^{-4} eV/K)
		78K	300 K	78K	300 K		
B.4	0.72	668	720	1.738	1.580	1.794	7.117
B.5	0.25	680	728	1.641	1.574	1.665	3.018
B.7	0.44	668	708	1.677	1.530	1.729	6.622
B.8	0.96	644	708	1.811	1.625	1.876	8.378
B.9	1.21	670	728	1.755	1.575	1.818	8.108

4. Conclusions

The investigated CdSe thin films are polycrystalline and exhibits a hexagonal structure. The crystallites are preferentially oriented with (002) plane parallel to the substrate surface.

The electrical conductivity was found to increase after the heat treatment. From the temperature dependence of electrical conductivity the thermal activation energy was determined. The studied samples have n-type conduction, determined by the donor levels of native defects.

From the photoconductivity spectra at 78 K and 300 K the coefficient of this temperature dependence was estimated to be about $3\text{-}8 \times 10^{-4}$ eVK^{-1}. Form absorption spectra and spectral dependence of photoconductivity, values between 0.22 and 0.29 μm were found for the diffusion length.

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