Journal of Optoelectronics and Advanced Materials Vol. 7, No. 2, April 2005, p. 817 - 821

ON THE OPTICAL PROPERTIES OF POLYCRYSTALLINE CdSe THIN FILMS

C. Baban[*], G. I. Rusu, P. Prepelita

Faculty of Physics, “Al. I. Cuza” University, Carol I Blvd, Iasi, R-700506, 11, Romania,

In this paper optical properties of CdSe thin films deposited by thermal evaporation under vacuum onto glass substrates are presented. The structural investigations performed by means of XRD technique showed that the films have a polycrystalline and hexagonal (würtzite) structure. The values of some important parameters of the studied films (absorption coefficient, optical bandgap energy and refractive index) are determined from transmission spectra. The values of the optical bandgap energy, E_g, calculated from the absorption spectra, ranged between 1.65 and 1.75 eV. The dispersion of the refractive index was explained using a single oscillator model.

(Received August 18, 2004; accepted March 23, 2005)

Keywords: CdSe, polycrystalline thin films, Optical properties, Refractive index

1. Introduction

Among II-VI semiconductor compounds CdSe is an important material for the development of various modern technologies of solid-state devices such as solar cells, high-efficiency thin-film transistors, light-emitting diodes, etc. [1].

In recent years major attention have been given to the investigation of electrical and optical properties of CdSe thin films in order to improve the performances of the devices and also for finding new applications [2-6]. CdSe thin films have been prepared using a variety of methods including physical vapour deposition, sputtering, spray pyrolysis, electrodeposition, etc [7-10]. The physical vapour deposition in its variants is often used because it offers many possibilities to modify the deposition parameters and to obtain films with determined structures and properties. Thermal evaporation under vacuum by using quasi-closed volume technique is one of the most advantageous methods for obtaining uniform CdSe films.

In present paper the influence of the preparation conditions on the optical properties of CdSe thin films is investigated.

2. Experimental

CdSe thin films were deposited on glass substrates by evaporating under vacuum the polycrystalline powder of the compound, using the quasi-closed volume technique [11]. The vacuum evaporation took place in a small cylinder chamber (8 cm high and 7 cm in diameter) in order to increase the vapor pressure of the components [12] (Cd atoms and Se_2 molecules) in the vicinity of the substrate. The substrate holder was placed horizontally on the top of this chamber and could be rotated (400 rot/min) around the cylinder’s axis.

The thin-film samples were prepared under various conditions: the temperature of the evaporation source, $T_{ev} = 900 – 1050$ K, the substrate temperature, $T_s = 290$-490 K, thus resulting a deposition rate, $r_d = 10 – 110$ Å/s.

The film thickness ($d = 0.10$-1.80 μm) was measured using an interferometric method (Fizeau’s method for fringes of equal thickness [13])

The structure of the films was analyzed using XRD technique, and the surface morphology of the films was investigated by means of AFM.

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[*] Corresponding author: baban@uaic.ro

Transmission spectra, in the spectral range 600-1400 nm, were recorded using an UV–VIS M–40 (C. Zeiss, Jena) spectrophotometer.

3. Results and discussion

The X - ray diffraction patterns (Fig. 1) indicate that the studied films are polycrystalline and have a hexagonal (würtzite) structure. The films are highly oriented with the (002) planes parallel to the substrate. Our investigations showed that the crystallite size ranged between 20 and 100 nm [14].

In Fig. 2 an AFM image typical for investigated samples is presented. The roughness of the film surface is small (RMS roughness is about 3 – 6 nm).

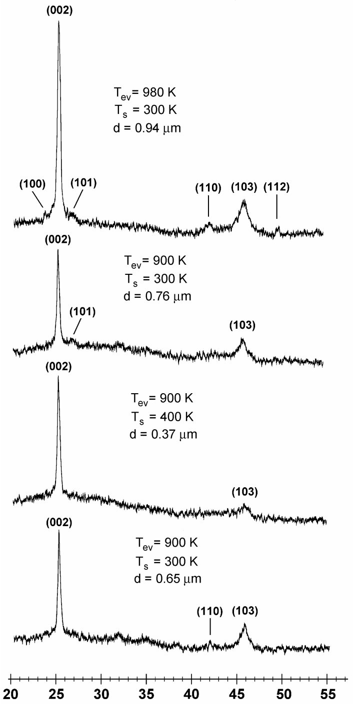

Fig. 1. XRD patterns of CdSe films obtained in different conditions.

It was found that the average size of the crystallites increases with increasing substrate temperature and the temperature of the evaporation source. A heat treatment (an annealing of films at 200 °C for 30 min) carried out after film deposition also determines an increase of the crystallite size.

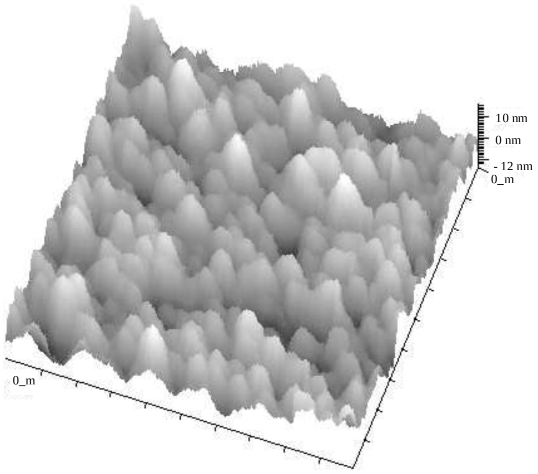

Fig. 2. AFM image for a CdSe film (d = 0.79 μm, T_{ev} = 1020 K, T_s = 300 K).

Fig. 3 shows typical transmission spectra for investigated films. Interference maxima and minima due to multiple reflections on film surfaces can be observed. This is in agreement with AFM investigations showing that the films have a good plane surface. A very rough surface will destroy the interference due to multiple reflections. For heat-treated samples the transmission coefficient is greater than before the heat treatment. This fact is due to the increase in the crystallite size observed for heat-treated samples.

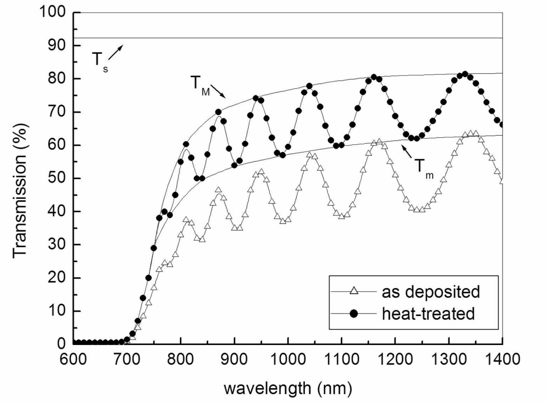

Fig. 3. Transmission spectra before and after the heat treatment and envelopes for minima (T_m) and maxima (T_M) (d = 1.6 μm, T_{ev} = 1050 K, T_s = 300 K).

From the transmission spectra the optical parameters of the films (absorption coefficient and refractive index) were calculated using Swanepoel's method [15]. The transmission coefficient for the film-substrate system, taking into account interference due to multiple reflections at the system interfaces is given by

$$T = \frac{A\tau}{B - C\tau\cos\varphi + D\tau^2} \tag{1}$$

where

$$\begin{array}{ll} A = 16n^2 n_s & D = (n-1)^3 (n - n_s^2) \\ B = (n+1)^3 (n + n_s^2) & \varphi = 4\pi n d / \lambda \\ C = 2(n^2 - 1)(n^2 - n_s^2) & \tau = \exp(-\alpha d) \\ & d = \text{thickness of the film} \end{array} . \tag{2}$$

The refractive index, n and the absorption coefficient, α of the film depend on the wavelength, λ. The refractive index of the substrate, n_s = 1.500 was determined from transmission spectra of the glass slides used as substrates.

The interference fringes are obtained when cosφ = ± 1 or

$$2nd = m\lambda \tag{3}$$

where m is an integer for maxima and a half integer for minima. The envelopes for maxima and minima are given by [15]

$$T_M = \frac{A\tau}{B - C\tau + D\tau^2} \qquad T_m = \frac{A\tau}{B + C\tau + D\tau^2} . \tag{4}$$

Finding this envelopes (see Fig. 3) offers the possibility to determine the wavelength dependence of refractive index and absorption coefficient by solving the equations (4) on a computer.

It was found that the absorption coefficient decreases after the heat treatment. Above the fundamental absorption edge the dependence of the absorption coefficient on the incident photon energy is determined by allowed direct transitions. The values of the optical bandgap energy, E_g, (1.65 - 1.75 eV) (Table I) [16,17] determined from absorption spectra are similar with the values reported for bulk CdSe [1].

Below the fundamental absorption edge it can be observed a tail in the absorption coefficient, which is a characteristic of most of the optical data on polycrystalline semiconductors [18]. The tail of the absorption spectra can be decomposed into a constant, wavelength independent part and an exponential Urbach part wich is considered to be determined mainly to the structural disorder existing at the grain boundaries [14].

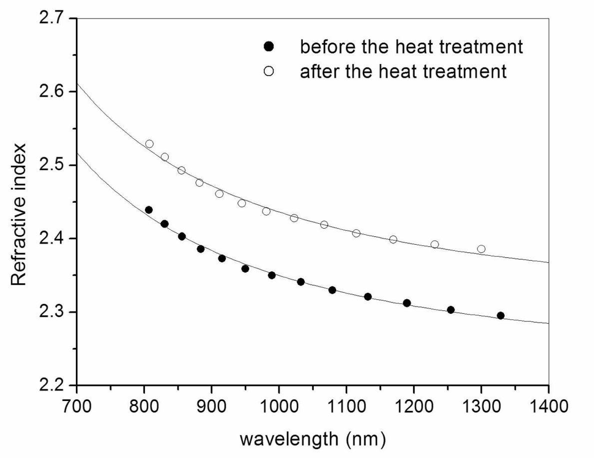

Fig. 4. Influence of the heat treatment on the refractive index.

The refractive index calculated using Swanepoel's method is presented in Fig. 4 as a function of wavelength. In this figure the points represents the calculated values of the refractive index. The refractive index was found to increase after the heat treatment probably due to the increase of the compactness of the films after the heat treatment simultaneously with the increase of the crystallite size. The dispersion of the refractive index is normal and it is well described by a single oscillator model. In Fig. 4 the lines represent the fitting of experimental points using the single oscillator model in the form proposed by Wemple and Di Domenico [19]

$$n^2 = 1 + E_d E_0 / [E_0^2 - (h\nu)^2] \tag{5}$$

were E_0 is the single oscillator energy, E_d is the dispersion energy and $h\nu$ is the photon energy. The values of these parameters are summarized in Table I. The value of the single oscillator energy is about twice the bandgap energy $E_0 \approx 2E_g$. For single crystals it was calculated [19] that the dispersion parameter is $E_d = 20.6$ while for our polycrystalline thin films we found a smaller value. The values of the dispersion parameter are increasing with the substrate temperature and also after the heat treatment.

Table 1. Optical parameters of some CdSe thin film samples.

T_s (K)	d (μm)	E_g (eV)	E_0 (eV)	E_0/E_g	E_d (eV)
300	0.72	1.730	3.536	2.04	15.97
300	0.96	1.740	3.468	1.99	14.89
300	1.21	1.672	3.391	2.03	13.47
300*	0.96	1.710	3.501	2.05	16.03
400*	0.77	1.726	3.584	2.08	16.34
500	1.73	1.668	3.476	2.08	14.97

* heat-treated samples

4. Conclusions

Polycrystalline CdSe thin films were prepared using the quasi-closed volume technique. The structure of the films consists of fine and highly oriented grains with hexagonal (002) planes parallel to the substrate. The crystallites size increases when the substrate temperature and the temperature of the evaporation source are increased. The transmission spectra are strongly influenced by the deposition conditions. A higher transmission coefficient is observed after a heat treatment. A direct optical band gap of 1.65 – 1.75 eV was found from absorption spectra. The tail of the absorption spectra is considered to be determined mainly by the structural disorder existing at the grain boundaries. The dispersion of the refractive index is normal and it is well described by a single oscillator model.

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