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2000 J. Phys.: Condens. Matter 12 7687

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## Optical properties of CdSe films deposited by the quasi-closed volume technique

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Received 31 January 2000, in final form 5 June 2000

**Abstract.** Polycrystalline CdSe thin films ( $d = 0.08\text{--}1.65\ \mu\text{m}$ ) have been prepared by the quasi-closed volume technique under vacuum on glass substrates. The film structure was studied by the x-ray diffraction technique and atomic force microscopy.

The values of the optical parameters (refractive index,  $n$ , and absorption coefficient,  $\alpha$ ) were determined from transmission spectra. The optical energy gap for the obtained CdSe films was also determined. The influence of deposition conditions (substrate temperature, evaporation source temperature) on the values of optical parameters is investigated.

### 1. Introduction

Cadmium selenide (CdSe) is one of the II–VI semiconductors that have been studied intensively in recent years [1–6]. This fact is due to its interesting properties and potential applications such as solar cells, high-efficiency thin-film transistors, electron-beam pumped lasers, light-emitting diode and electroluminescent devices, etc [6–10].

A variety of methods for preparation of CdSe films have been reported by different authors, like chemical vapour deposition, sputtering, electrodeposition and vacuum evaporation [4–11]. Both electrical and optical properties [7–14] have been studied, and it is very clear that these properties are very sensitive to deposition conditions.

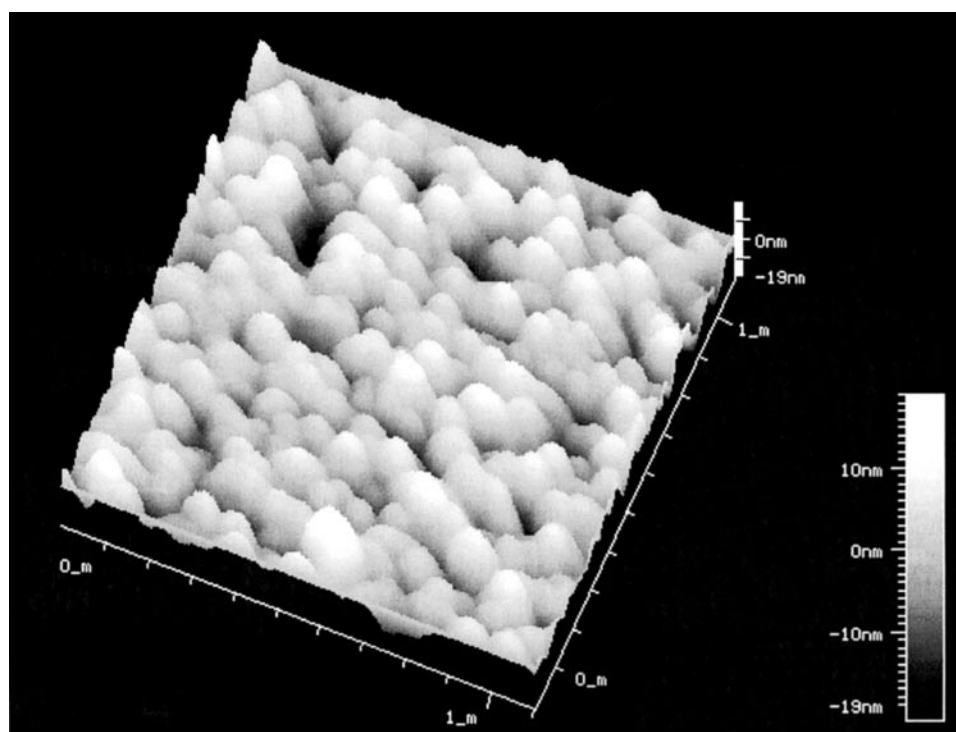
In this paper some optical properties (transmission spectra, absorption coefficient, refractive index) of CdSe thin films are investigated as a function of deposition conditions.

### 2. Experiment

CdSe thin films were prepared by physical vapour deposition of CdSe polycrystalline powder (99.99% purity) under vacuum, at a pressure of less than  $10^{-5}$  Torr. The films were deposited onto cleaned glass substrates placed at a distance of approximately 10 cm from the vapour source.

The quasi-closed volume technique was used. This method takes into account the complete dissociation of CdSe into Cd and  $\text{Se}_2$  molecules during the evaporation process [11]. When arriving at the substrate, Cd and  $\text{Se}_2$  particles must also become absorbed in the proper ratio and recombine to form CdSe compound. An incomplete recombination of the components on the substrate may lead to non-stoichiometric films [9–11]. The films with Cd or Se excess can be established by measuring the optical transmission [9–11].

The experimental arrangement and deposition technique used for preparation of CdSe thin films are described in [15].



**Figure 1.** AFM image of a CdSe film ( $d = 1.60 \mu\text{m}$ ,  $T_s = 290 \text{ K}$ ,  $T_{ev} = 1040 \text{ K}$ ,  $r_d = 107 \text{ A s}^{-1}$ ).

Samples for x-ray diffraction (XRD) and optical measurements were simultaneously deposited. X-ray patterns of samples were taken by using Co  $K\alpha$  radiation. The surface structure of the films was investigated by means of atomic force microscopy (AFM).

The experimental arrangement permitted us to prepare the films under various conditions: the deposition rate,  $r_d$ , ranged from 9 to  $110 \text{ \AA s}^{-1}$ , the substrate temperature,  $T_s$ , was varied between 290 and 400 K and the temperature of the evaporation source,  $T_{ev}$ , ranged between 900 and 1050 K.

The thickness of the films was measured by the multiple-beam Fizeau fringe method [9] and for the investigated samples ranged between 0.08 and  $1.65 \mu\text{m}$ .

Our investigations showed that the deposited films have a polycrystalline structure. For studied samples the average size of the crystallites determined by means of AFM ranged between 20 and 100 nm. The crystallite size increases with increasing film thickness, substrate temperature during deposition and deposition rate.

The heat treatment after film deposition also determines an increase of the crystallite size.

In figures 1 and 2 are presented AFM images for two investigated samples. We remark that the grains have similar size and shape. The presence of pin holes in the studied films is not observed. A detailed discussion on the polycrystalline structure of our investigated films is presented in [16].

Transmission spectra were obtained using a Specord UV-VIS double beam spectrophotometer (C Zeiss, Jena), at room temperature.

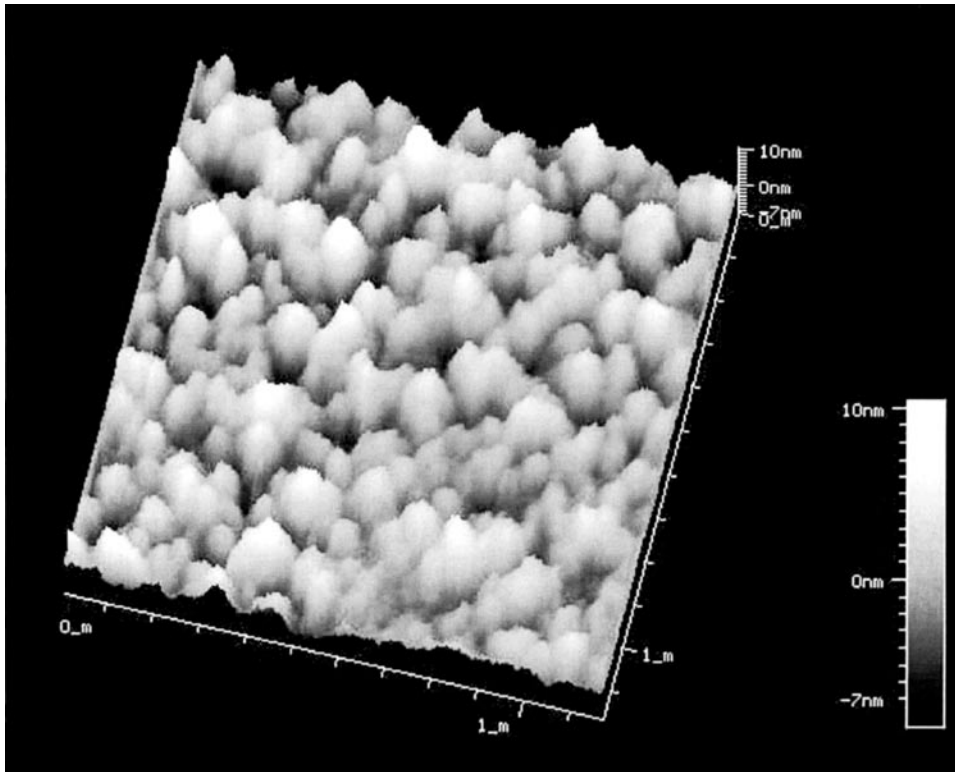


Figure 2. AFM image of a CdSe film ( $d = 0.90 \mu\text{m}$ ,  $T_s = 290 \text{ K}$ ,  $T_{ev} = 1000 \text{ K}$ ,  $r_d = 60 \text{ A s}^{-1}$ ).

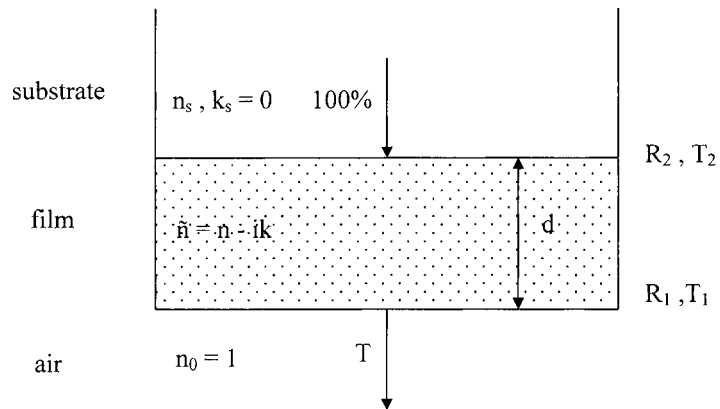


Figure 3. Schematic representation of film-substrate system.

### 3. Theoretical considerations

The thin-film-substrate system used for optical measurements is schematically presented in figure 3.

The CdSe film has a thickness  $d$  and a complex refractive index  $\tilde{n} = n - ik$ , where  $n$  is the refractive index and  $k$  the extinction coefficient. The substrate is considered transparent

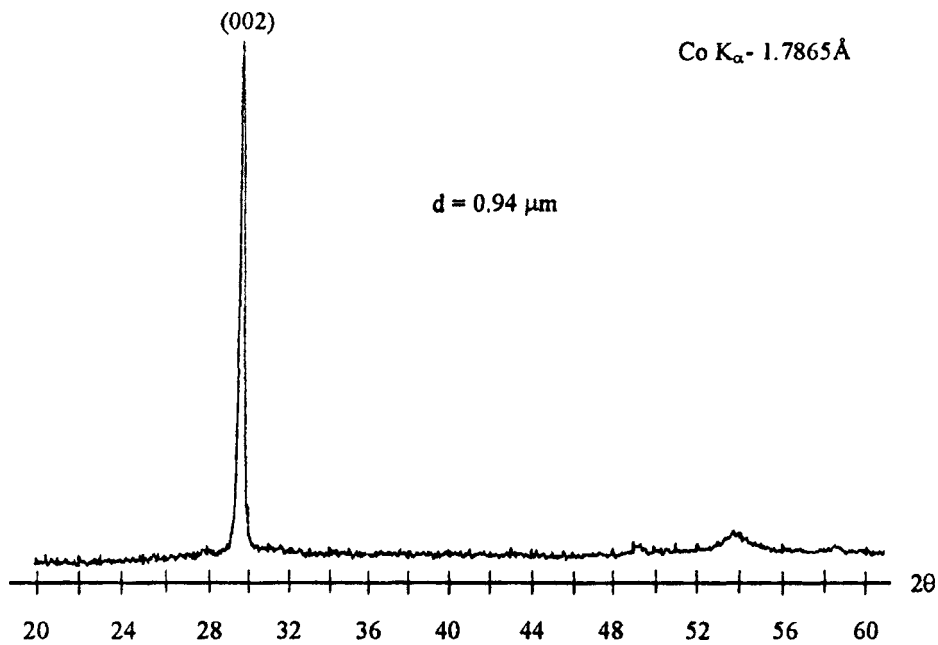


Figure 4. X-ray diffraction pattern for a CdSe thin film with a thickness of 0.94  $\mu\text{m}$ .

( $k_s = 0$ ) and its refractive index is  $n_s$ , (figure 3). The thickness of the substrate is several orders of magnitude larger than  $d$ .

The reflection coefficients,  $R_1$  and  $R_2$ , and transmission coefficients,  $T_1$  and  $T_2$ , for the two interfaces, air–film and film–substrate respectively, are given by the following expressions [17]:

$$R_1 = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} = 1 - T_1 \quad R_2 = \frac{(n-n_s)^2 + k^2}{(n+n_s)^2 + k^2} = 1 - T_2. \quad (1)$$

In our experiments the optical transmission  $T$  for the film–substrate systems (figure 1) was measured compared with the optical transmission of a glass substrate. Thus  $T$  is the optical transmission for the film in the semi-infinite substrate approximation. If the thickness of the film is constant, the transmission coefficient,  $T$ , and the reflection coefficient,  $R$ , due to the film, taking into account multiple reflections and interference effects, are given by [18]

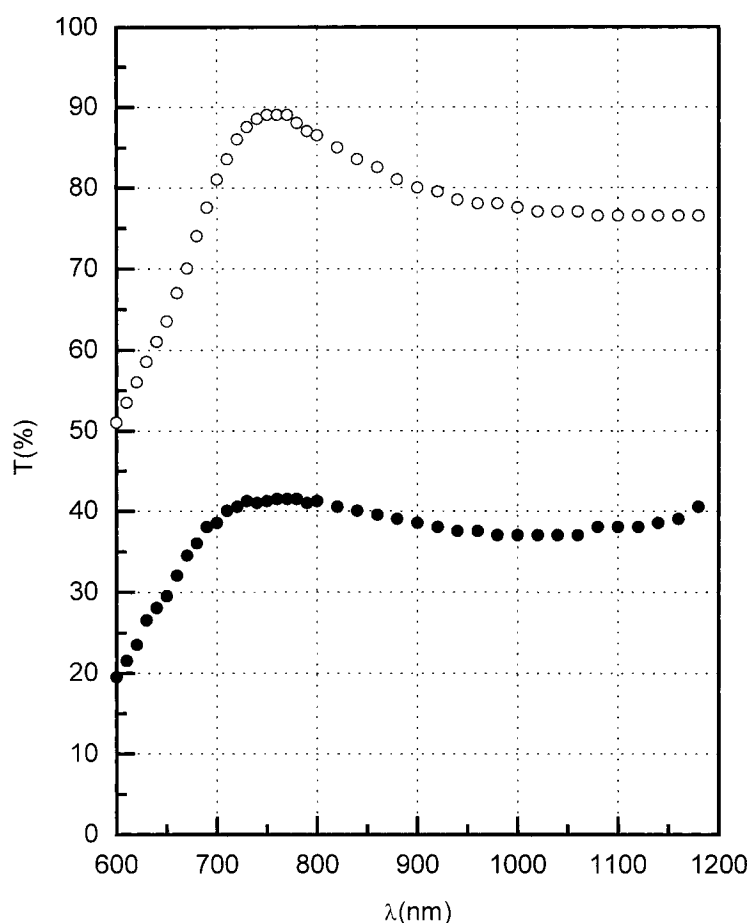
$$T = \frac{T_1 T_2 \tau}{1 - 2\sqrt{R_1 R_2} \tau \cos \varphi + R_1 R_2 \tau^2} \quad (2)$$

$$R = \frac{R_1 - 2\sqrt{R_1 R_2} \tau \cos \varphi + R_2 \tau^2}{1 - 2\sqrt{R_1 R_2} \tau \cos \varphi + R_1 R_2 \tau^2} \quad (3)$$

where  $\tau = \exp(-\alpha d)$  ( $\alpha = 4\pi k/\lambda$  is the absorption coefficient) and  $\varphi = 4\pi n d/\lambda$ . If  $2nd = m\lambda$ , where  $m$  is an integer (half integer) a maximum (minimum) in the transmission spectra is obtained.

#### 4. Results and discussion

The x-ray diffraction patterns for CdSe films indicate (as seen from figure 4) that the samples are polycrystalline and have a wurtzite (hexagonal) structure. The crystallites are preferentially oriented with the (002) planes parallel to the substrate.



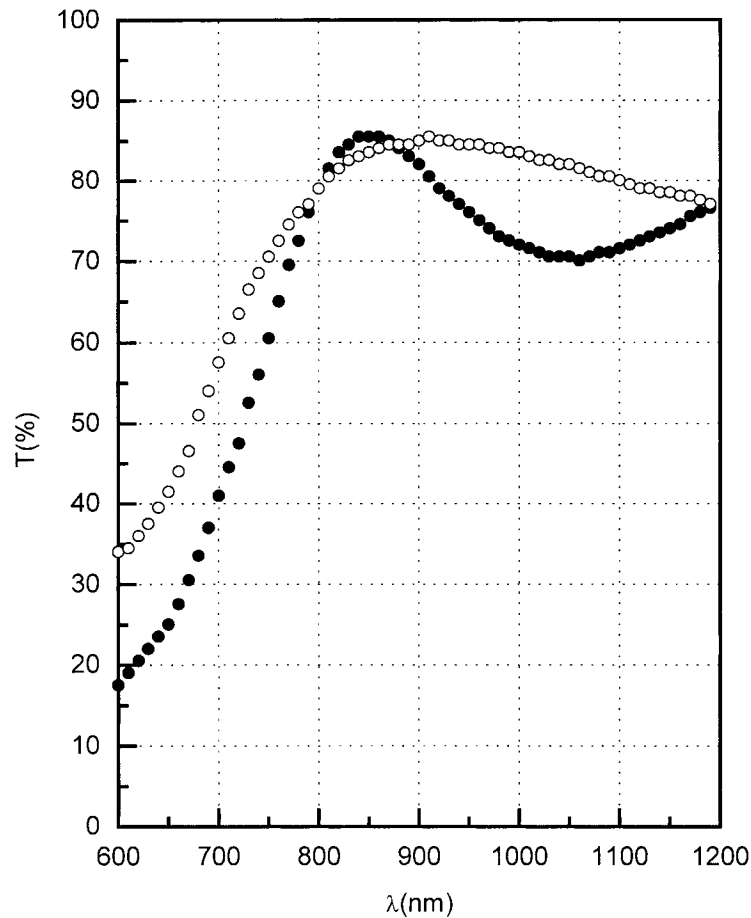
**Figure 5.** The transmission spectra for a CdSe film with  $d = 0.32 \mu\text{m}$ , before (●) and after (○) the heat treatment.

In previous papers [15, 19–26] we studied the temperature dependence of the electrical conductivity and Seebeck coefficient of a great number of semiconductor materials (Te, CdTe, CdS,  $\text{Bi}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ , organic semiconductors etc) in thin films. It was experimentally established that the stable structure and normal stoichiometry of the films can be obtained if (after deposition) they are submitted to a heat treatment, consisting of several successive heatings and coolings within a certain temperature range,  $\Delta T$ , characteristic for each sample. After these heat treatments the temperature dependence of the electrical conductivity and Seebeck coefficient become reversible.

Our samples were subjected to a heat treatment within a temperature range 300–500 K. The rate of heating and cooling was about  $2.5^\circ\text{C min}^{-1}$ . For CdSe films the shapes of temperature dependence of the electrical conductivity during heat treatment are presented in [16].

The influence of the heat treatment on the shape of the transmission spectra is shown in figure 5 for one sample. Similar behaviours were noticed for the other samples under study.

It can be observed that for the heat-treated sample the transmission coefficient is greater than before the treatment. This fact is probably due to the increase in the crystallite size.



**Figure 6.** The transmission spectra for heat-treated CdSe films: (●)  $d = 0.76 \mu\text{m}$ ,  $T_s = 290 \text{ K}$ ,  $T_{ev} = 930 \text{ K}$ ,  $r_d = 63 \text{ A s}^{-1}$ ; (○)  $d = 0.18 \mu\text{m}$ ,  $T_s = 290 \text{ K}$ ,  $T_{ev} = 900 \text{ K}$ ,  $r_d = 9 \text{ A s}^{-1}$ .

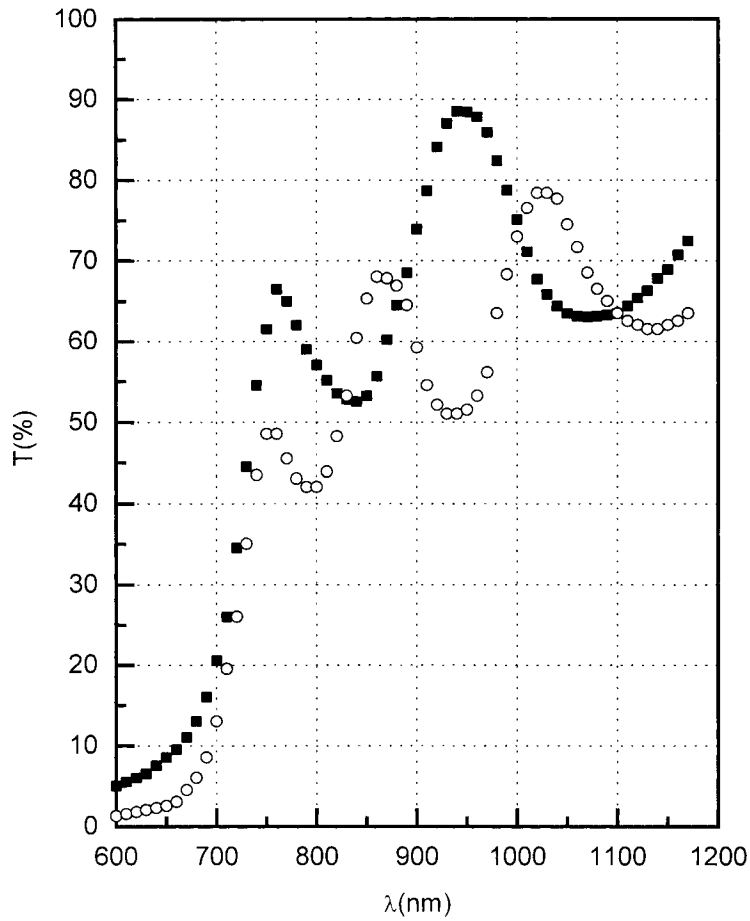
The intercrystalline boundaries contain structural defects, impurities etc. These factors might influence the absorption processes.

Figures 6 and 7 illustrate the transmission spectra for four heat-treated samples. The experiments showed that transmission coefficient strongly depends on the film structure, which is determined by the film thickness and its deposition conditions.

A sharp absorption edge at a wavelength that corresponds to the forbidden energy gap indicates that the films have a stoichiometric composition.

The number of the interference fringes in the transmission curves is determined by the thickness of the film. For two films with a greater thickness the transmission curves are presented in figure 7. For respective samples the refractive index, in the spectral domain of the medium and strong transmission, is calculated using the Swanpoel method [27] of creating envelopes of the interference maxima and minima. The envelope function is taken as  $y = c_1 + (c_2 + c_3x)^{1/2}$  in order to construct smooth envelopes [28]. Firstly an approximate value of refractive index is calculated using the expression which can be obtained from (2) [10, 27, 28]

$$n_1 = [N + (N^2 - n_s^2)^{1/2}]^{1/2} \quad (4)$$



**Figure 7.** Typical transmission spectra for CdSe films with greater thickness: (■)  $d = 0.77 \mu\text{m}$ ,  $T_s = 290 \text{ K}$ ,  $T_{ev} = 1000 \text{ K}$ ,  $r_d = 65 \text{ A s}^{-1}$ ; (○)  $d = 0.04 \mu\text{m}$ ,  $T_s = 400 \text{ K}$ ,  $T_{ev} = 1000 \text{ K}$ ,  $r_d = 87 \text{ A s}^{-1}$ .

where

$$N = 2n_s \frac{T_{max} - T_{min}}{T_{max}T_{min}} + \frac{2n_s^2 + 1}{2}. \quad (5)$$

In this last expression  $T_{max}$  and  $T_{min}$  are the transmission maximum and minimum at the same wavelength, one being measured and the other calculated with the envelope function. The value of the refractive index of the glass substrate is determined by relationship [28]

$$n_s = \frac{1}{T_s} + \left( \frac{1}{T_s^2} - 1 \right)^{1/2} \quad (6)$$

where  $T_s$  is the optical transmission for the substrate only.

With this value of the refractive index of the film the 'order'  $m$  of the different extremes of the transmission curve is determined with the equation for interference fringes

$$2n_1d = m\lambda \quad (7)$$

In our case the thickness of the film,  $d$ , was known.



**Table 1.** Refractive index of the sample with  $d = 0.77 \mu\text{m}$ .

$\lambda$ (nm)	$n_1$	$m$	$m_0$	$n$
760 (maximum)	2.635	5.34	5	2.467
840 (minimum)	2.613	4.79	4.5	2.445
940 (maximum)	2.524	4.13	4	2.441
1070 (minimum)	2.476	3.56	3.5	2.431

**Table 2.** Refractive index of the sample with  $d = 1.04 \mu\text{m}$ .

$\lambda$ (nm)	$n_1$	$m$	$m_0$	$n$
755 (maximum)	2.656	7.32	7	2.541
795 (minimum)	2.638	6.90	6.5	2.484
860 (maximum)	2.621	6.34	6	2.481
935 (minimum)	2.594	5.77	5.5	2.472
1025 (maximum)	2.534	5.14	5	2.465
1135 (minimum)	2.407	4.41	4.5	2.455

The values of  $m$  are then approximated to the close integer or half integer  $m_0$  [28]. These values of  $m_0$  are used to determine the new value of the refractive index  $n$  from the same relation (6). The values of  $n$  for the two samples are listed in tables 1 and 2.

Nearly at the absorption edge the absorption coefficient can be calculated using the expression [9]

$$\alpha = \frac{1}{d} \ln \frac{1}{T}. \quad (8)$$

The fundamental absorption may be due either to allowed direct transitions described by the well known relation [10, 11, 17],

$$\alpha h\nu = A_a (h\nu - E_g)^{1/2} \quad (9)$$

or to forbidden direct transitions described by

$$\alpha h\nu = A_f (h\nu - E_g)^{3/2} \quad (10)$$

where  $h\nu$  is the incident photon energy,  $E_g$  represents the energy bandgap and  $A_a$  and  $A_f$  are characteristic parameters, independent of photon energy, for respective transitions.

The analysis of our experimental data shows that for all samples the dependences of  $(\alpha h\nu)^2$  as a function of the photon energy  $h\nu$ , indicates the direct nature of fundamental band-to-band transitions. This means that CdSe films have a direct bandgap energy, which is in accordance with the energy band models proposed for hexagonal CdSe [29]. This is confirmed by plotting  $(\alpha h\nu)^2$  against  $h\nu$  (figures 8 and 9). The values of bandgap width,  $E_g$ , have been determined by extrapolating the linear portions of the respective curves to  $(\alpha h\nu)^2 = 0$ . For the investigated samples these values ranged between 1.70 and 1.80 eV, which is in good agreement with the values obtained for bulk CdSe [1–3, 10, 17, 30–32].

The values of bandgap energy are found to decrease with the increase of the film thickness.

A characteristic of most of the optical data on polycrystalline semiconducting films is an additional absorption for photon energies less than the bandgap energy [10, 33]. The shape of this additional absorption generally depends on the grain size. At higher photon energies the shape of absorption curves is less sharp in polycrystalline compared

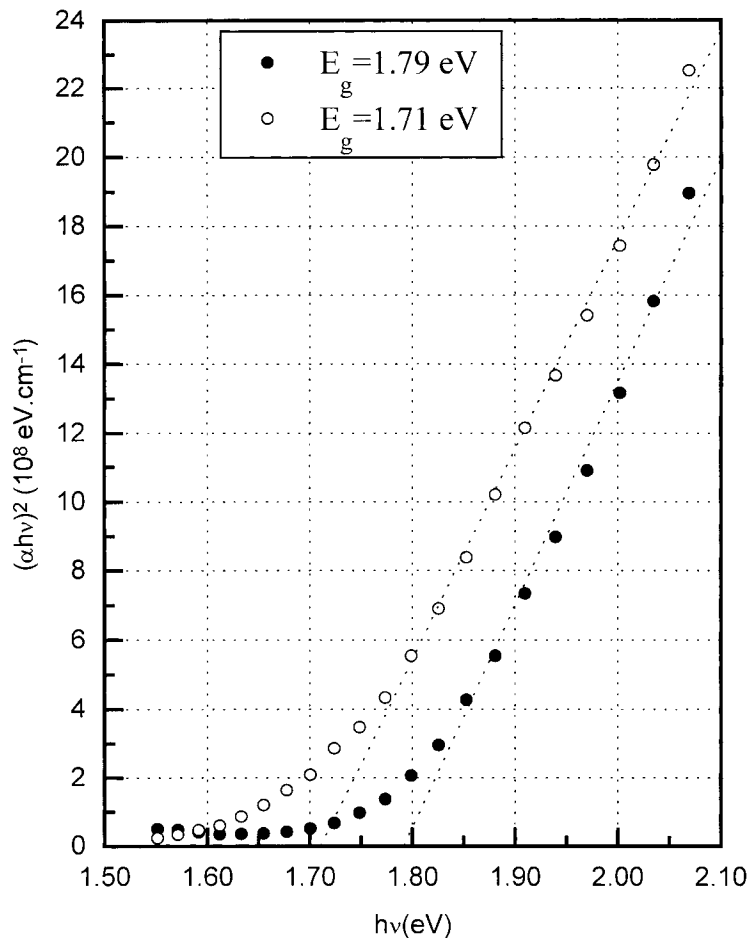


Figure 8.  $(\alpha h\nu)^2$ -photon energy  $h\nu$  plots for CdSe films: (●)  $d = 0.32 \mu\text{m}$ , (○)  $d = 0.76 \mu\text{m}$ .

to crystalline semiconducting films [10, 33–35]. We used an experimental technique for measuring transmission spectra, which permitted us to obtain good values of optical parameters in the vicinity of the fundamental absorption edge.

It is well known that in polycrystalline thin films transport phenomena are strongly influenced by crystallite size and the characteristics of grain boundaries [9, 10]. From this reason the determination of the energy gap from the temperature dependence of the electrical conduction is difficult. In these cases other mechanisms of charge transfer such as hopping conduction, impurity band conduction etc may be active. For our CdSe films the value of the thermal activation energy determined from the temperature dependence of the electrical conduction is about 0.15 eV [16].

The evaluation of the energy gap from optical absorption seems to be more appropriate.

## 5. Conclusions

The investigated CdSe thin films obtained by vacuum evaporation onto glass substrates revealed a polycrystalline structure. The crystallites are preferentially oriented with (002) plane parallel

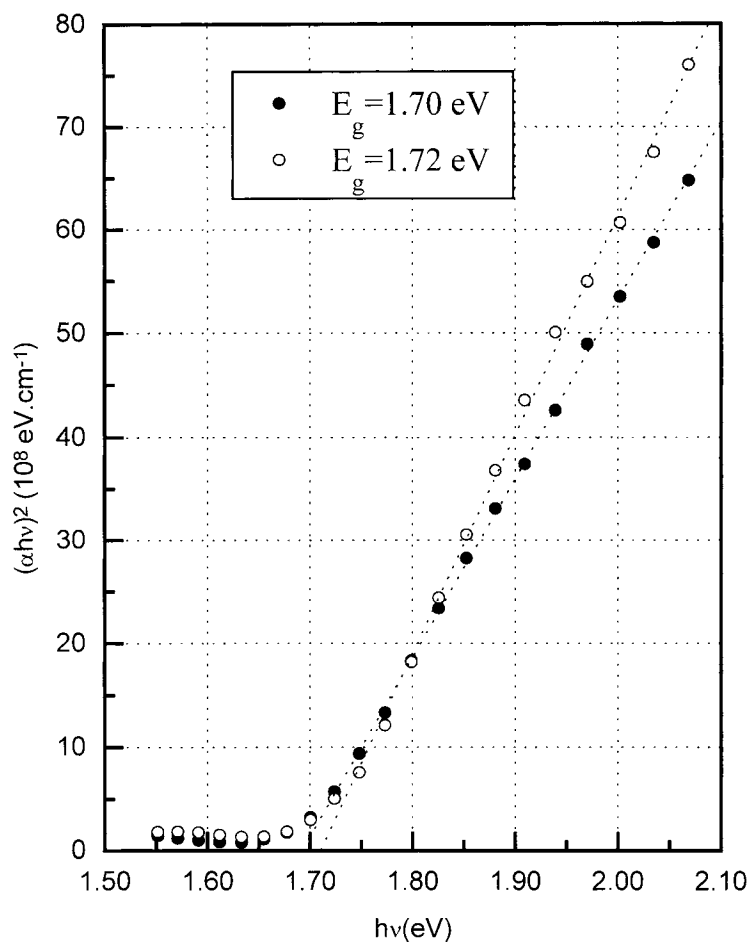


Figure 9.  $(\alpha hv)^2$ -photon energy  $h\nu$  plots for CdSe films: (●)  $d = 0.77 \mu\text{m}$ , (○)  $d = 1.04 \mu\text{m}$ .

to the substrate surface. The shape of the transmission spectra is strongly influenced by the preparation conditions of films and heat treatment. The spectral dependence of the refractive index indicates a normal dispersion. The values of energy gap, calculated from the absorption spectra, range between 1.70 and 1.80 eV.

### Acknowledgments

The authors would like to thank Mr M Morariu for providing AFM images of some studied samples.

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