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ON THE ELECTRICAL AND OPTICAL CHARACTERISTICS OF CdO THIN FILMS

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Cadmium Oxide (CdO) thin films (d=0.15 μm - 0.70 μm) were deposited by thermal evaporation under vacuum onto glass substrates kept at 300 K and 473 K respectively. Depending on the substrate temperature, films with polycrystalline or amorphous structures were obtained. The influence of substrate temperature and post-deposition heat treatment on the electrical conductivity, σ, and optical transmittance in visible region was investigated. An irreversible temperature dependence of σ during heating/cooling cycles of as-grown samples was observed. The results are discussed in relation with cadmium excess and the film recystallization during annealing process. The optical energy bandgap ($E_g \cong 2.4$ eV) determined from absorption spectra, indicates direct interband transitions.

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1. Introduction

Cadmium Oxide (CdO) thin films are regarded as a material with many attractive properties such large energy bandgap, high transmission coefficient in visible spectral domain, remarkable luminescence characteristics etc.

In the last ten years, the electrical and optical properties of CdO thin films prepared by various techniques such as spray pyrolysis, oxidation of cadmium films, chemical vapour deposition etc. have been studied. It was experimentally established that these properties are very sensitive to the film structure and deposition conditions [1-5].

In present paper the electrical properties (temperature dependence of electrical conductivity) and optical properties (transmission and absorption spectra) of CdO thin films evaporated in vacuum by quasi-closed volume technique are investigated.

2. Experimental

CdO thin films where deposited onto glass substrates by physical vapour deposition of CdO polycrystalline power using the quasi-closed volume technique. The deposition equipment is described in detail in [6]. The substrate temperature, T_S, during film deposition was varied between 300 K and 475 K; the temperature of the evaporation source, T_{ev} , was 1100 K;, the source - substrate distance was 12 cm; and the deposition rate was about 10 Å/s.

The thickness, *d*, measured with an interference microscope, ranged between 0.09 μm and 0.70 μm. The film structure was studied by X-ray diffraction (XRD) technique using the CoK_α radiation (λ = 0.1790 nm).

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The temperature dependence of electrical conductivity, σ, in the temperature range 300 K-575 K was studied using surface type cells. Indium thin films (d=1.0 - 2.0 *μm)* deposited in vacuum onto CdO films after their preparation, were used as ohmic contacts (electrodes).

The reflection and transmission spectra (in the spectral range 400 nm-1350 nm) were recorded using an *Steag Eta-Optik* spectrometer. The absorption coefficient, α , was determined from the relation [7]:

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R_\lambda)^2}{T_\lambda}\right], \tag{1}$$

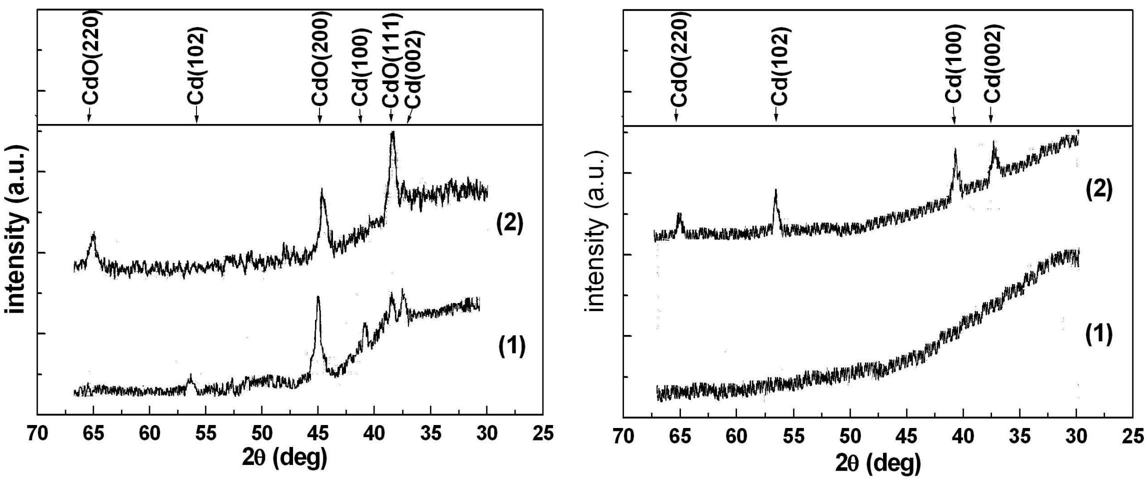
where d denotes films thickness and R_λ and T_λ are the reflection and transmission coefficient, respectively, at wavelength λ.

Some samples were subjected to a heat treatment consisting in a heating/cooling cycle, under ambient conditions, at room temperature to final 575 K at ratio 6 K/min. An isochronal annealing arrangement was used.

3. Results and discussion

3.1 Structural characteristics

In Fig. 1a,b the representative XRD patterns for CdO thin films deposited at different substrate temperatures are presented. The pattern (1) from Fig. 1a corresponds to as-growth films deposited onto unheated substrates and reveals a nanocrystalline structure of the film. In this diffraction pattern, the peaks at 2Θ 38.3° and 44.5° correspond to diffraction from (111) and (200) planes of the CdO cubic phase, respectively [8]. It can be also observed that the respective diffraction pattern exhibits additional peaks at 2Θ $\cong$ 37.3°, 40.6° and 56.5°. These peaks correspond to the (002), (100) and (102) planes of the Cd crystalline phase and indicate that in respective films there is small amount of unoxidized Cd grains mixed with oxide. After the heat-treatment, the film structure is improved. A significant increase of peak intensities corresponding to (100), (200) and (220) planes of CdO take place (Fig. 1a, pattern 2). This indicates the formation of nearly stoichiometric CdO films during annealing process.



(a) (b)

Fig. 1. XRD patterns (CoK$_\alpha$ radiation) of CdO thin films deposited at substrate temperature of 300 K (a) and 473 K (b); (1) – before, (2) -.after heat treatment at 573 K.

For the as-deposited CdO films evaporated onto heated substrates (T_S = 473 K), the diffraction pattern shows an amorphous structure (Fig. 1b). After heat treatment, the structure of such films becomes polycrystalline (Fig. 1b, pattern 2). The peaks located at $2\Theta \cong 37.3^o$, 40.6^o and 56.5^o in XRD pattern indicate that the film exhibits a Cd excess which precipitates as a consequence of the annealing process.

These structural characteristics of the evaporated CdO thin films influence their electrical and optical properties.

3.2 Electrical properties

The temperature dependence of the electrical conductivity of the studied films during successive heating/cooling cycles are studied in temperature range 300 K-575 K.

Figs. 2 and 3, depict the $ln\sigma$ versus the inverse of temperature for the CdO films deposited at different substrate temperatures.

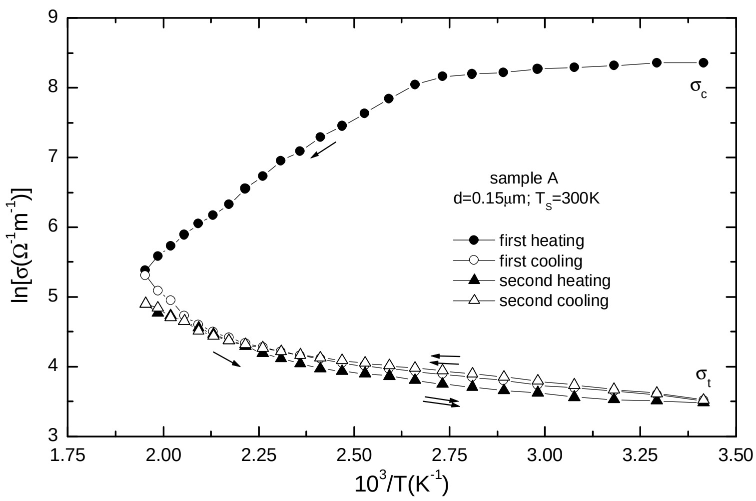


Fig. 2. Typical temperature dependence of the electrical conductivity during heating/cooling cycles for CdO films deposited at 300 K.

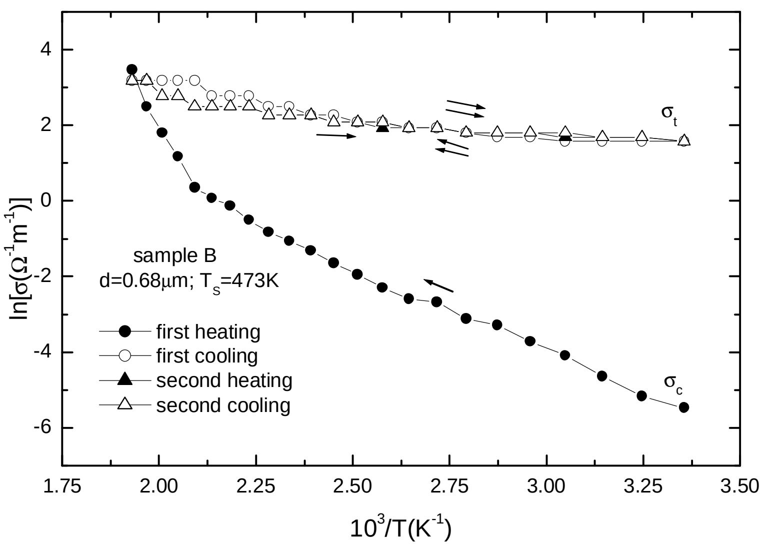


Fig. 3. Typical temperature dependence of the electrical conductivity during heating/cooling cycles for CdO films deposited at 473 K.

As it results from Fig. 2, for the films deposited onto unheated substrate, the electrical conductivity, σ, remains practically constant at the beginning of the first heating up to about 365 K. This may due to excess of cadmium atoms which determine a metallic characteristics of the electrical conductivity. With increasing of the temperature, σ start to significantly decrease fact that can be explained by oxidation of Cd atoms from intercrystallite domains. The decrease of peak intensities corresponding to Cd in the XRD pattern for such heat treated films (Fig. 1a) confirm this supposition. The reversible dependence of the σ in the next heating/cooling cycles indicates the stability of the film structure after annealing.

For the CdO films deposited at 473 K, the temperature dependence of σ is also irreversible (Fig. 3). But in this case, σ increases irreversible during first heating. After first cooling, the temperature dependence of σ becomes reversible. We suppose that this behavior is determined by removal of oxygen atoms from the amorphous film during their crystallization and by aggregation of Cd excess as a consequence of the film annealing. Both these processes determine an irreversible increasing of electrical conductivity of the respective films.

Similar irreversible temperature dependence of σ was observed for other semiconducting materials in thin films as CdTe [9,10] and In_2O_3 [11].

In Table 1 are given the values of electrical conductivity at room temperature, before (σ_c) and after (σ_t) heat treatment for films deposited at different substrate temperatures. It can be observed the strong dependence of σ_c on deposition conditions and also the noticeable changes of σ during heat treatment.

Table 1. Electrical conductivity at room temperature, before (σ_c) and after (σ_t) heat treatment.

sample	d(μm)	T_S(K)	$\sigma_c(\Omega^{-1}m^{-1})$	$\sigma_t(\Omega^{-1}m^{-1})$
A	0.15	300	5.3×10^4	3×10
B	0.68	473	3.7×10^{-3}	4.8

3.3 Optical properties

Optical properties of CdO thin films are also influenced by the deposition conditions. In Figs. 4 and 5 the optical transmission spectra in the wavelength range 400-1350 nm for as-grown and annealing samples deposited at 300 K and 473 K are shown.

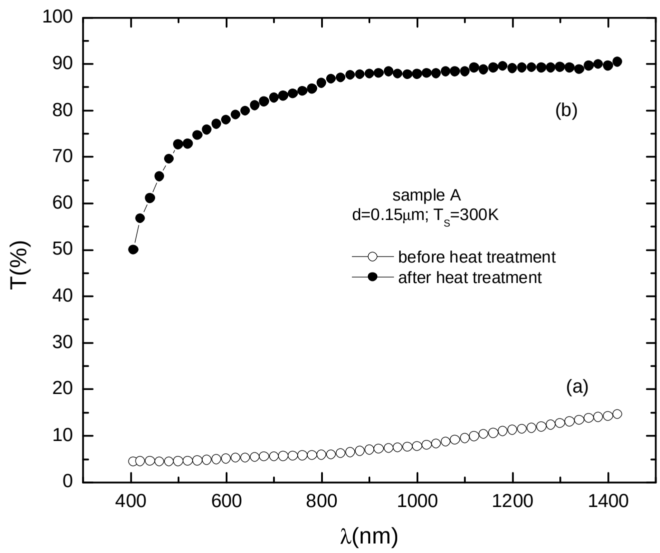


Fig. 4. Effect of heat treatment on the optical transmittance of CdO thin films deposited at 300 K.

As it may be seen (Fig. 4a) the optical transmittance of the sample A deposited at room temperature is very lower before heat treatment in comparison with transmittance of sample deposited at 473 K (Fig. 5a). This fact may be attributed to presence in the sample A of Cd microcrystallites which have a greater absorbance in the visible region. The decrease of the Cd excess during the film annealing and improvement of the film crystallinity explain the significantly increasing of transmittance sample A (Fig. 4,b). The film deposited onto heated substrate have high transmittance and the heat treatment determines a small decrease of transmittance due the Cd precipitation in the transition from amorphous to polycrystalline structure (Fig. 5,b).

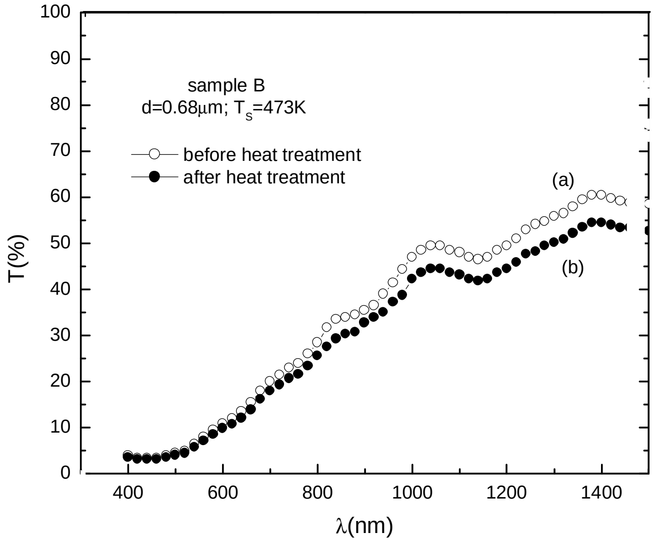


Fig. 5. Effect of heat treatment on the optical transmittance of CdO thin films deposited at 473 K.

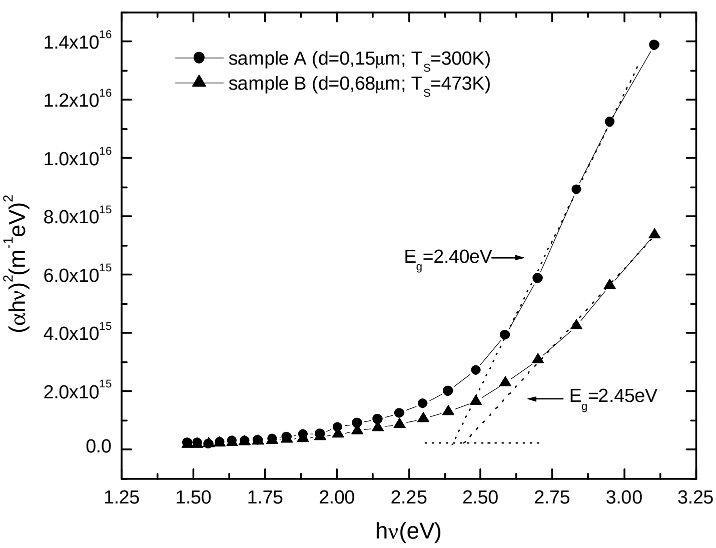


Fig. 6. The dependence $(\alpha h\nu)^2 = f(h\nu)$ corresponding to samples from Figs. 4 and 5.

The CdO is a material with a direct band gap lying in the range: 2.2-2.7 eV [12]. For such band to band transitions the dependence of absorption coefficient α versus photon energy is given by the relations [13]:

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g)^{1/2}, \quad (2)$$

where A is a parameter independent of $h\upsilon$ and E_g is the optical band gap energy. Ploting the dependence of $(\alpha h\upsilon)^2$ vs. $h\upsilon$, the value of E_g can be determined by extrapolating the linear portion of this plot to $(\alpha h\nu)^2 = 0$. Such plots for representative heat treated samples are shown in Fig. 6. The obtained values of E_g , (2.40 eV and 2.45 eV) are in good agreement with those reported for CdO thin films prepared by other techniques [3,5].

4. Conclusions

Thin films of cadmium oxide have been evaporated by quasi-closed volume technique onto glass substrates kept at 300 K and 473 K, respectively.

The influence of substrate temperature and heat treatment on the structure, electrical conductivity and transmission spectra was investigated. It was established that the as-grown CdO films deposited at room temperature exhibit a nanocrystalline structure with Cd excess, whereas those deposited at 473 K are amorphous. The heat treatment improves the film crystallinity and decreases the Cd excess.

The temperature dependence of electrical conductivity during heating/cooling cycles is irreversible in first cycle due to the Cd excess. The heat treatment determine a reversible $ln\sigma = f(1/T)$ dependence and an increasing of optical transmittance in visible region.

The obtained values for optical energy gap, E_g, around 2.4 eV indicate the direct nature of fundamental band-to-band transitions in the studied CdO films.

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