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On the structural characteristics of thermally oxidized CdO thin films

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In the paper, the structural characteristics of CdO thin films (d = 340 – 400 nm) obtained by thermal oxidation of evaporated metallic Cd thin films are investigated. Cd thin films were deposited in vacuum onto unheated glass substrates at source temperature of 770 K. The as-deposited Cd thin films were heat treated in ambient conditions with different heating rates and at various temperatures ranged between 300 K and 650 K. By XRD and AFM techniques the crystalline structure and surface morphology both for the as-deposited Cd films and the thermal oxidized CdO thin films are studied. The obtained results are correlated with the oxidation process that takes place during film annealing.

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1. Introduction

In the last years, binary semiconducting oxides (SnO_2, ZnO, In_2O_3, CdO, Ga_2O_3 etc) in thin films are considered as important functionally materials that possess superior properties in a wide range of conditions and have a great number of interesting applications (gas sensors, solar cells, ultrasonic oscillators, photodiodes, etc). From these oxides, cadmium oxide (CdO) thin films have received considerable attention due to their attractive properties such as large energy band gap, high transmission coefficient in visible spectral domain, high electrical conductivity, remarkable luminescence characteristics etc. Like to other oxides thin films, the physical properties of CdO thin films are very sensitive to their preparation conditions and different post-deposition treatments. Various deposition methods such as DC sputtering, magnetron sputtering, pulsed laser sputtering, spray pyrolysis, activated reactive evaporation, sol-gel, chemical bath deposition, etc. have been employed to obtain different oxide thin films, particularly for CdO thin films [1-5]. Another technique used for preparation of oxide thin films is the thermal oxidation of metallic thin films. Such method was successfully used to obtain zinc oxide [6– 8], tin oxide [9], indium oxide [10, 11] etc. thin films. An important factor which influences the structure and physical properties of the as oxidized thin films is the heating rate during oxidation process. Also, the annealing temperature plays a significant role in determining of the physical properties of thermal oxidized thin films [11, 12].

In present paper, the thermal oxidation technique was used to obtain CdO thin films. The effect of oxidation conditions on the structural characteristics and surface morphology of as prepared CdO thin films have been investigated.

2. Experimental

The studied CdO thin films (d=340-400nm) were obtained as follows: firstly, the metallic Cd thin films were evaporated in vacuum, at room temperature, onto pre-cleaned glass substrates, with 1.5x1.5 cm^2 area. During deposition, the Cd source temperature was kept constant at 770 K. After deposition, the obtained in the same conditions Cd thin films were divided in two groups: first group was subjected to a gradual heating in air with the rate of 5 K/min. up to temperatures of 560 K and 650 K respectively, maintained at respective temperatures for 5 min. The second group was directly subjected to the temperature of 650 K (flash heating) for 5 min.

During Cd film heating, its color varied from silver-gray at room temperature to black-brown at temperature of 560 K and to red color at temperature of 650 K.

The structural characterization was performed by X-ray diffraction (XRD) using the CuK_α radiation (λ = 1.5418 Å). The atomic force microscope (AFM) in the tapping mode was used to study the surface topography of the films.

3. Results and discussion

In Fig. 1 the typical patterns for both as-deposited and thermally oxidized Cd films are shown. From respective XRD patterns one can conclude that both evaporated Cd thin films and those thermal oxidized were polycrystalline. The XRD pattern for as-deposited Cd films is characterized by a strong peak at $2\theta = 31.9^o$ (Fig.1 a) which corresponds to (002) plane of the hexagonal Cd structure [13]. This indicates that in respective films, the crystallites grow preferential with (002) plane parallel to the substrate. The average Cd grain size in direction of c-axis, calculated using Sherrer formula [14], was found of about 30 nm.

Table 1. d- film thickness, T_a –annealing temperature, θ_{111} - diffraction angle corresponding to (111) planes, TC (hkl)-texture coefficient for various planes;

Sample	d (nm)	T_a (K)	$2\theta_{111}$(deg)		TC(hkl)				
			Standard	Experimental	(111)	(200)	(220)	(311)	(222)
Z.1 (gradually oxidized)	365	560	33.03	33.08	1.84	0.40	0.29	0.34	2.11
Z.2 (gradually oxidized)	360	650	33.03	33.15	2.02	0.22	0.21	0.20	2.33
Z.3 (flash-oxidized)	370	650	33.03	33.14	1.95	0.21	0.20	0.16	2.48

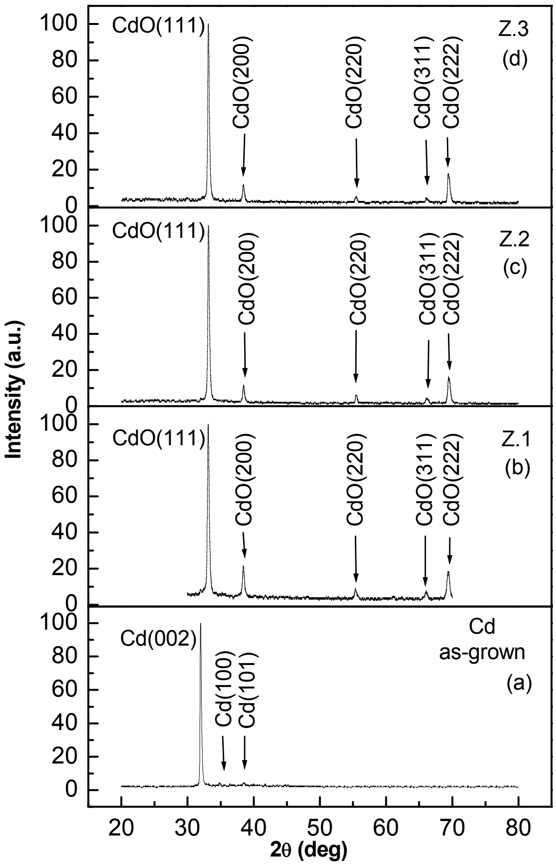

Fig. 1. Typical XRD patterns for studied films:(a) – as-grown Cd films; (b), (c) – CdO thin films gradually oxidized up to temperature of 560 K (sample Z1) and 650K (sample Z2), respectively; (d) – CdO films obtained by flash-oxidation at temperature of 650 K (sample Z3).

The typical XRD patterns recorded for Cd films after their heating with various rate are shown in Fig.1 (b-d). As can be seen, the respective patterns exhibit the diffraction peaks characteristic to the CdO faces centered (FCC) cubic structure [15]. This reveals that CdO was formed during Cd film annealing.

The strong intensity of the peaks at 2θ = 33.1° from each pattern shows that the (111) preferred orientation is characteristic for all respective CdO films. The about same aspect of the XRD patterns from Fig. 1(b-d) indicates that the heating of the CdO film from 560 K to 650 K or the increase of heating rate (from gradual to flash heating) do not significantly influence the crystalline structure of the as obtained CdO films. This shows that the oxidation of metallic Cd films begins at a temperature lower than 560 K or that the film oxidation is a relative fast process.

The values of some structural parameters determined for analyzed CdO samples are summarized in Table 1 and Table 2.

The texture coefficient TC(hkl) which describes the preferred orientation of the crystallites in respective samples was calculated using the expression [16, 17]:

$$\mathrm{TC(hkl)} = \frac{\mathrm{I(hkl)/I_0(hkl)}}{\mathrm{N^{-1}\sum I(hkl)/I_0(hkl)}} , \qquad (1)$$

where TC(hkl) is the texture coefficient of the (hkl) plane, I and I_0 denote the measured and ASTM standard intensities of the (hkl) maxima, respectively, and N is the number of the reflections in diffraction patterns. From Table 1 one can be seen that the calculated values of TC(hkl) are deviated from unity, especially those corresponding to (111) and (222) planes. This indicates that the respective films have the largest preferred crystallographic orientation along the (111) diffraction plane, which increase with annealing temperature. Such higher values for the texture coefficient have also reported by F.C. Eze for reactive vacuum evaporated CdO films deposited at various partial pressure of oxygen [18]. So, one can conclude that in both cases (of CdO films obtained by thermal oxidation of vacuum evaporated Cd films and of those obtained by reactive vacuum evaporation) occur similar growth mechanism of the CdO crystallites.

Using the well-known Bragg formula [14] the lattice parameter "*a*" for CdO cubic structure was evaluated for each diffraction planes from Fig. 1 (b-d). The obtained values ranged between 4.68 Å and 4.69 Å and are light lower than standard value of 4.695 Å [15]. This indicates the presence of the compressive stress in the films, produced by different factors as impurities, lattice defects, vacancies, deformation faults, etc [14, 19, 20]. The shift towards higher 2θ values of the diffraction maxima relative to their normal positions, as it results from Table1, confirms above assumption. Similar shift of the diffraction maxima have been also noticed by other authors for CdO thin films prepared by spray pyrolysis [21, 22] and reactive vacuum evaporation [18] being attributed to the lattice contraction. Also, the oxygen vacancies can be responsible for the lower value of lattice parameter [23]. The true value, a_0 , of lattice parameter for our typical CdO samples have been determined by plotting of lattice parameter calculated for each peak from XRD patterns versus the function Nelson-Riley (NRF) defined by the expression [17, 21, 24]:

$$\mathrm{NRF}=\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right) , \qquad (2)$$

where θ is the Bragg angle.

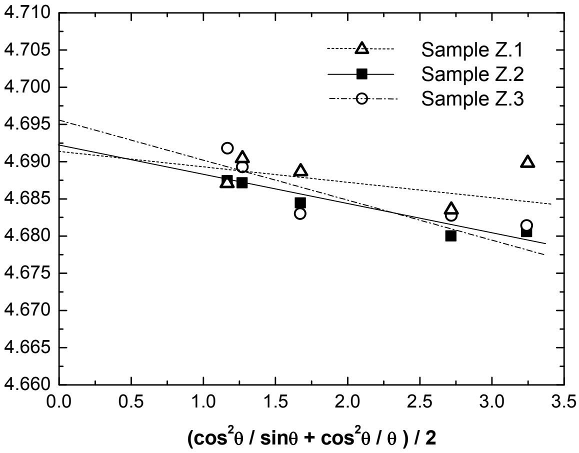

Fig. 2. Nelson-Riley plots of lattice parameter for typically studied CdO samples.

Fig 2. shows the "*a*" versus NRF plots obtained for the analyzed CdO samples. By extrapolating of the lines to NRF = 0, the true lattice parameter, a_0, for respective CdO films were obtained. The summarized values from Table 2 are very close to those for bulk CdO and suggest the good crystalinity of the films, especially for those flash oxidized.

The information on the average crystallite size, *D*, as well as the microstrain, ε, for analyzed CdO samples, were obtained using the equation [5, 14]:

$$\beta=\frac{\lambda}{D\cos\theta}+\varepsilon\tan\theta \ , \qquad (3)$$

where β is the full-width at half-maxima (FWHM) of the diffraction peak and λ denotes the wavelength of X-radiation.

Fig 3 shows the plots of βcos θ versus sin θ for various planes for typical studied samples. From the intercept of the lines with y axis the crystallite sizes *D* was calculated.

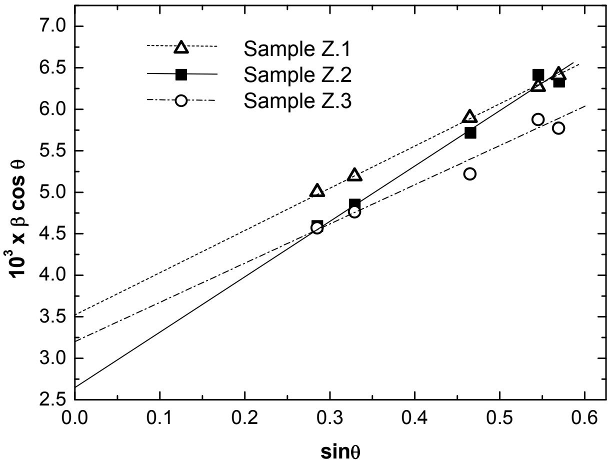

Fig. 3. Plot of β cos θ vs. sin θ for typical studied CdO thin films.

Also, the average strain, ε, in the film was determined from the slope of the graph. The obtained results are listed in Table 2.

Table 2. a_o - lattice parameter, ε – average strain, D- average crystallite size, r_a and r_{rms} – roughness Parameters.

Sample	a_0 (Å)	ε (10^{-3})	*D* (nm)	r_a (nm)	r_{rms} (nm)
Z.1 (gradually oxidized)	4.6 91	5.1	43	54.6	70.9
Z.2 (gradually oxidized)	4.692	6.6	58	36.1	46.0
Z.3 (flash-oxidized)	4.695	4.7	48	37.1	47.7

One can see that for gradually heated CdO samples, *D* slowly increases with increasing of annealing temperature from 560 K to 650 K. This can be ascribed to the increase of oxygen content in the film grain as consequence of the oxidation of non-oxidized yet cadmium atoms. Comparing the values of crystallite size from Table 2 one can conclude that the flash-heating of the Cd film determines the formation of CdO grains with lower size compared with those for gradually oxidized samples. This result is in concordance with AFM micrographs for respective samples from Fig. 4.

Regarding the values of ε, one can seen that the increase of annealing temperature from 560 K to 650 K determines an increase of the microstrain. This fact can be also attributed to the increase of oxygen content in the film. For the flash oxidized CdO sample the microstrain increasing is not so significantly. The obtained values for ε agree well with those reported relative to the vacuum evaporated CdO thin films [17] and for CdO films deposited by spray-pyrolysis [21,22].

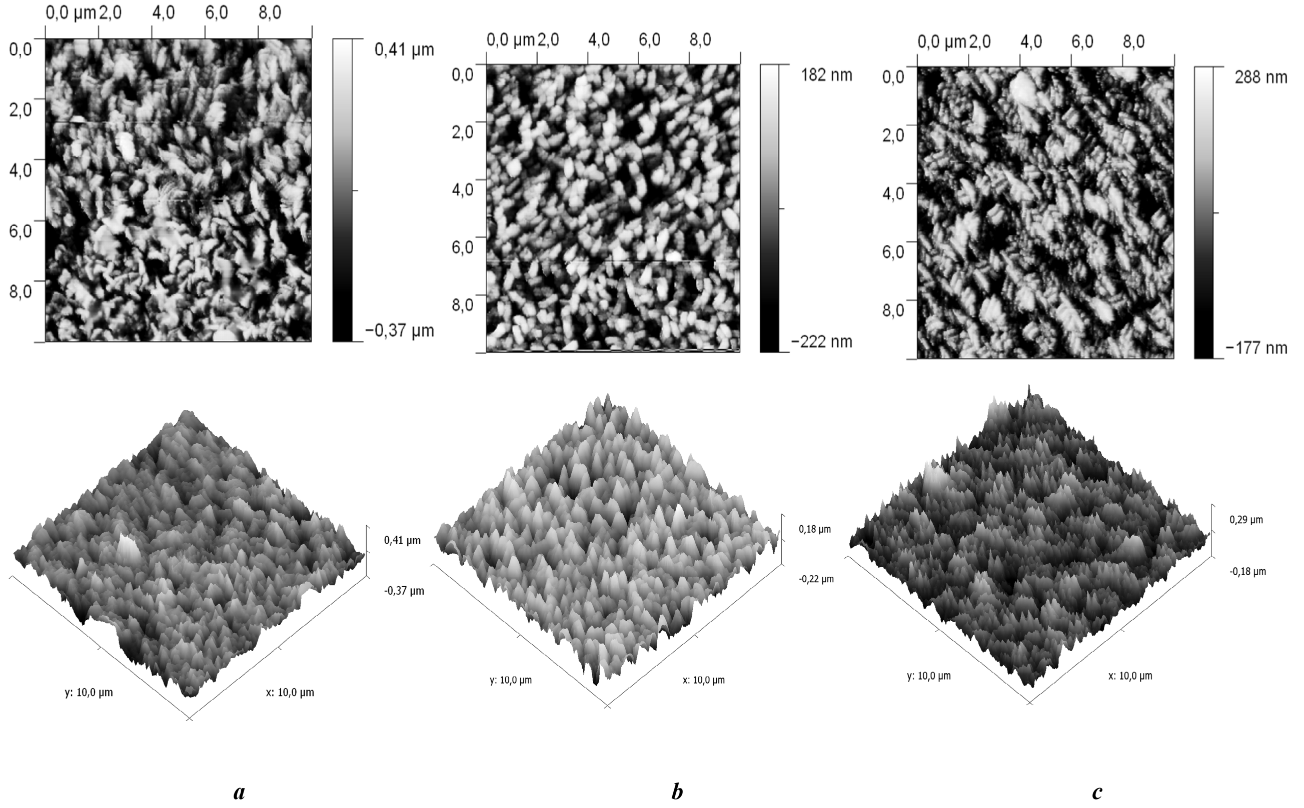

Fig. 4. AFM images for CdO studied films: (a), (b) – CdO thin films gradually oxidized up to temperature of 560 K (sample Z1) and 650K (sample Z2), respectively; (c) – CdO films obtained by flash-oxidation at temperature of 650 K (sample Z3)

Fig. 4 depicts a selection of (10 μm x 10 μm) 2D and 3D AFM images of the typical studied CdO thin films. One can observe that the surface of gradually oxidized samples contain a large number of pyramidal shaped hillocks distributed on the film surface, more homogenously in the case of the sample heated up to higher temperature. The flash oxidation of the Cd thin films determines the partially grain interlinking and the formation of the higher aggregates having smaller grains.

Some quantitative data about the surface roughness of the typical studied samples are summarized in Table 2. The about same values of roughness parameters obtained both for gradually and flash-oxidized samples, respectively, are in concordance with the previous conclusion relative to the similarity of their crystalline structures as it results from Fig. 1 (c,d).

4. Conclusions

Polycrystalline Cd thin films were evaporated in vacuum onto glass substrates at Cd source temperature of 770 K. By post deposition heating up to temperature of 650 K, by two manners (gradually and flash oxidized, respectively) CdO thin films were obtained. By means of XRD and AFM techniques, the structural characteristics of the typical obtained CdO samples have been investigated. The XRD study revealed that both typical CdO thin films present a polycrystalline cubic structure with (111) preferred orientation.

Some structural parameters like the crystallite size and average strain were determined for typical studied films. The obtained results revealed that these parameters have relatively higher values for gradually oxidized CdO films comparative to those of flash oxidized samples.

The AFM investigations have been shown that the surface roughness parameters have about the same values for both typical CdO studied films.

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