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The effect of annealing temperature on the structural and electrical properties of ultrasonically sprayed cadmium oxide films

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In this work, the effect of the thermal annealing on the structural and electrical properties of CdO films obtained by ultrasonic spray pyrolysis technique was studied. Samples were annealed at 250, 350 and 450 °C. X-ray diffraction patterns were taken, and texture coefficient (P), grain size (D) and dislocation density (δ) were calculated to explain the structural variations. Van der Pauw and Hall measurements were made, and electical resistivity and mobility values were calculated. It was determined from all investigations that the films had better structural and electrical characteristics after annealing processes.

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1. Introduction

Optoelectronic technology which is continuously developing and searching for innovations needs alternative transparent conducting oxide (TCO) materials with better physical characteristics. So, the investigation of the effect of thermal annealing on the characteristics of CdO films has great importance. TCO films are of technological importance for solar cells, chemical sensors and liquid crystal displays [1, 2]. Thin film solar cells require at least one of the contacts, typically the front, to be transparent [3]. CdO is one of the promising transparent conducting oxides with its unique physical properties [4, 5]. CdO thin films have been used in wide variety of applications such as photodiodes, phototransistors, photovoltaic cells, transparent electrodes, IR dedectors and anti reflection coatings [6, 7].

In this work, CdO films have been produced by USP technique and the structural and electrical properties of the films have been studied as a function of the annealing temperature for 250, 350 and 450 °C.

2. Experimental details

Ultrasonic spray pyrolysis (USP) technique which is economical and simple has been used to produce the CdO films. Details of the USP technique were given in our previous works [8, 9]. 0.1 M of $Cd(CH_3COO)_2.2H_2O$ solution has been prepared, and 200 ml of solution has been sprayed onto pyrex glass substrates (previously heated to 300 °C) during 40 mins. CdO films have been exposed to three different annealing temperatures as 250, 350 and 450 °C. The samples are named as A0 (not annealed), B1 (annealed at 250 °C), B2 (annealed at 350 °C) and B3 (annealed at 450 °C). The thicknesses of the films have been measured by a computer controlled Leitz PMM 12106 thickness gauge. The structural properties of the films have been studied by an x-ray diffractometer (XRD) (Rigaku Model, λ=1.5418 Å) with CuK_α radiation. The electrical properties have been investigated by Van der Pauw technique, and carrier concentration and mobility values were obtained by Hall experiment.

3. Results and discussion

3.1 Structural properties

XRD patterns of all films are given in Fig. 1. The crystallinity levels and some structural properties of CdO films have been investigated using these patterns. It is clear from XRD patterns that annealing improved the crystalline structure; make the peaks narrower and sharper. Harris analysis has been performed to determine the texture coefficient (P) using the equation below [10];

$$P(h_ik_il_i) = \frac{I\,(h_ik_il_i)}{I_0\,(h_ik_il_i)}\left[\frac{1}{n}\sum_{i=1}^{n}\frac{I(h_ik_il_i)}{I_0\,(h_ik_il_i)}\right]^{-1} \qquad (1)$$

where I_0 represents the standart intensity (ASTM, American Society of Testing Materials), I is the observed intensity of $(h_ik_il_i)$ plane and n is the reflection number. Fig. 2 (a) shows the P values of the films for three most intensive peaks on them. It is clearly seen that CdO_2 phase in the films became lower with increasing annealing temperature. The preferential orientation for annealed samples is (111) CdO. So, CdO_2 phase is unstable and (111) CdO phase becomes dominant with thermal process. We think that bounded but unstable oxygen in CdO_2 phase displaced in the film.

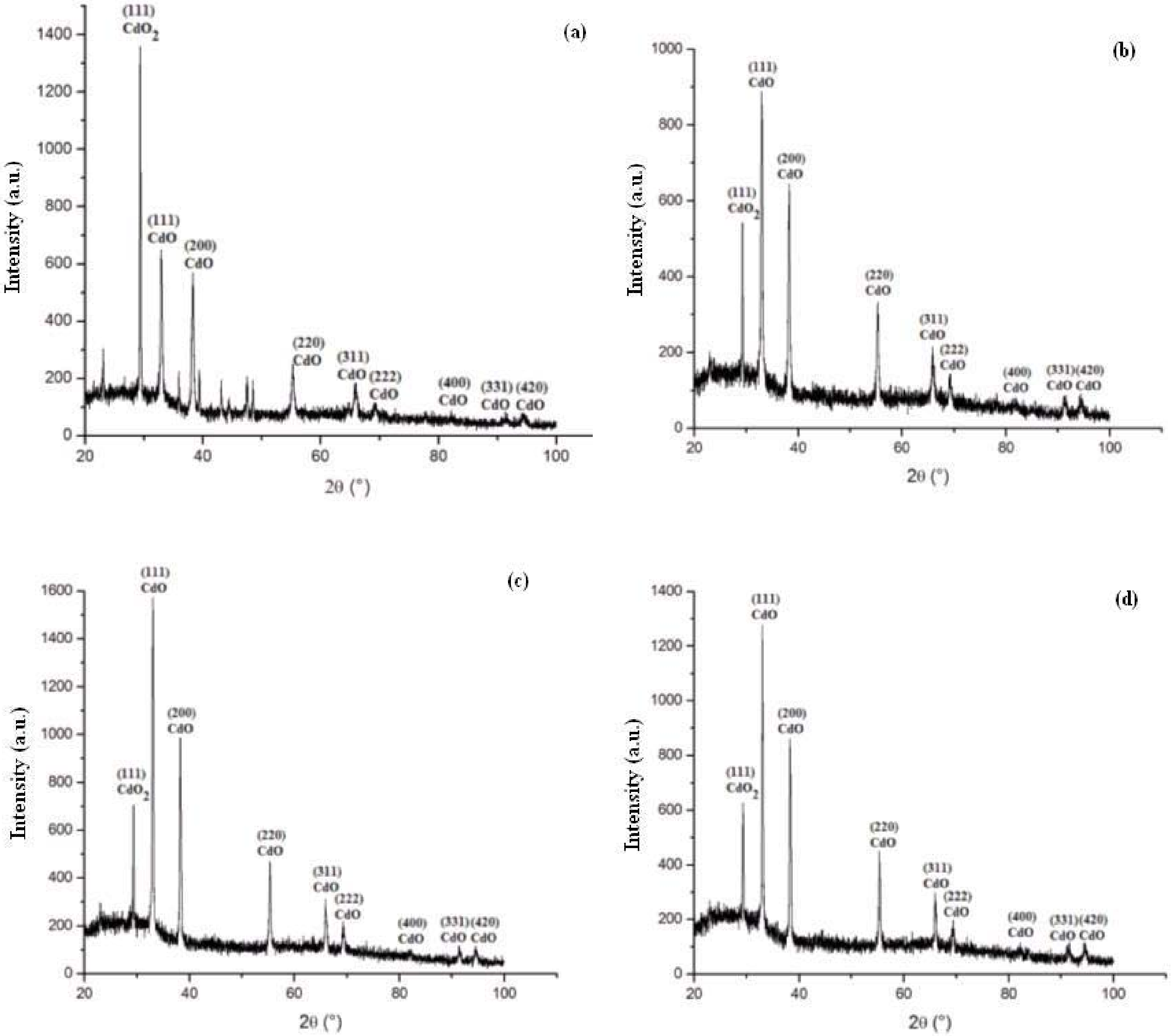
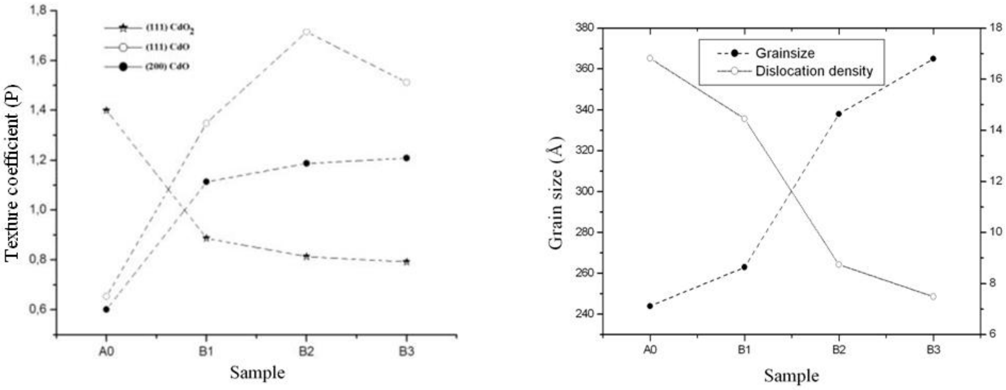


Fig. 1. XRD patterns of CdO films. a)A0(as deposited) b)B1 (annealed at 250°C) c)B2 (annealed at 250 °C) d) B3 (annealed at 250 °C).



(a) (b)

Fig. 2. (a) Texture coefficient (P) values (b) Grain size and dislocation density values of CdO films.

Grain sizes have been calculated for the preferential orientation (111) CdO using Scherrer formula [3];

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

where β is the half peak width as radian of the peak which has maximum intensity, D is the grain size, θ is the Bragg angle and λ is the wavelength of light used. The dislocation density (δ) also calculated using the formula given by Williamson and Smallman [2];

$$\delta = \frac{1}{D^2} \tag{3}$$

These values with other structural parameters such as 2θ and β are given in Table 1. Fig. 2 (b) shows the variation of grain size and dislocation density of the films by thermal annealing. It is clear from Fig. 2 (b) that grain size increases and dislocation density decreases by thermal annealing. Finally, we can say that thermal annealing has an important developing effect on the structural properties of CdO films and can be used to increase the quality of samples.

Table 1. Some structural and electrical parameters of CdO films.

Sample	2θ (°)	$\beta \times 10^{-3}$ (rad)	P	D (Å)	d (μm)	σ $(\Omega\ \text{cm})^{-1}$	μ $(\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1})$	$\delta \times 10^{-6}$ (line/nm^2)
A0	32.94	6.20	0.653	244	2.00	1.92	0.245	16.82
B1	32.92	5.74	0.653	263	1.25	1.724	0.336	14.45
B2	33.00	4.47	1.349	338	1.08	204.1	1.45	8.74
B3	33.04	4.13	1.716	365	1.05	454.5	9.572	7.49

3.2 Electrical properties

For the electrical characterization of the films, Van der Pauw and Hall measurement have been performed, and the electrical conductivity and mobility values have been calculated. Fig. 3 shows the variation of the electrical conductivity (σ) and mobility (μ) by thermal annealing. It is clear from this figure that thermal annealing (especially at 450 °C) has an important effect on the electrical properties. With thermal annealing, the structure becomes more stable and purified from defects. Also, we think that the oxygen which locates in to the grain boundaries and forms defects states for electrons goes out of these regions and finds areas to locate where it becomes electrically active. Decreasing of defects causes the mobility to increase. Because the effects such as lattice scattering and grain boundary scattering which would decrease the mobility are no more dominant in the structure. Table 1 shows the thicknesses (d), electrical conductivity (σ) and mobility (μ) values of the films. Our samples became more conductive films with high mobility values. This is a desired characteristic for various optoelectronic applications.

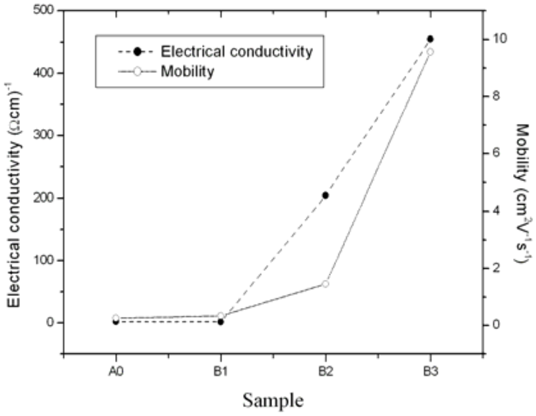


Fig. 3. Electrical conductivity and mobility values of CdO films.

3. Conclusion

In this work, CdO films have been produced by USP technique, and their physical characteristics have been tried to be improved by thermal annealing. Samples have been subjected to three different annealing temperatures as 250, 350 and 450 °C in air, and structural and electrical properties of the films have been investigated. After all investigations, thermal annealing ensured positive improvements on the film structure. We think that annealed samples will improve the characteristics of optoelectronic devices. Especially, low defect states and high electrical conductivity with increased mobility make annealed B3 sample a better candidate than as-deposited CdO film for technological applications.

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