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An effect of supporting electrolyte based CdO polycrystalline thin film prepared by electrodeposition method

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Abstract : The present workis aimed to deposit CdO thin film on FTO substrate with various bath temperatures by electro deposition technique. The CdO was chosen due to its high electrical conductivity, good optical transparency and moderate refractiveindex. Using X-ray diffraction analysis, the multifaceted properties such as macro and microstructural parameters have been found in prepared thin films at room temperature and 350˚C.It reveals that all the reflectionpeaks are good agreement with cubic structure and polycrystalline in nature.The optical properties of prepared thin films are determinedusing UV-visible and Photoluminescence spectroscopic (PL) techniques. A strong emission peak is exhibited at 420 nm (2.95eV) in the visible region.Scanning Electron Microscopy image showedan improvement of surface morphology with respect to the bath temperature and an addition of electrolyte.
Key words: CdO Thin film, Electrodeposition, Photoluminescence Spectra, FTIR.

Introduction

During past few decades, the nano material based metal oxides are emerging as significant materials for their versatile application such as photovoltaic solar cells, phototransistors, gas sensors and other optoelectronic devices[1]. An effort of research groups, the multiple semiconductors including tin oxide, zinc oxide, and indium oxide are still widely used for developing optoelectronic devices. Due to unique electrical and optical feature, CdO is noticed as a crucial n-type semiconductor with low band gap, high transmission coefficient and moderate refractive indices[2-5]. To synthesis and fabricate optoelectronic devices so far, different techniques have been employed for preparing CdO thin film which are hydrothermal method[6], RF magnetron sputtering [7], chemical both deposition[8], sol-ge[9], electron beam evaporation technique[10], electrodeposition method[11]. Among the above process, electrodeposition technique is used in the present work for the preparation of cadmium oxide thin films with respect to bath temperature. Because this method has received immense advantages such as low cost, high growth rate at low temperature and control shape and size of thin films. Further, the structural, morphology and luminescence characteristic of as prepared and annealed CdO thin films discussed in detail.

Experimental

The aqueous solution of 0.02 M cadmium nitrate tetra hydrate was used to prepare $Cd(OH)_2$ and CdO thin films on FTO substrate without and with supporting electrolyte KCL at different bath temperature. Three conventional electrodes potentiostate electrodeposition technique (Princeton Applied Research Model 362) was used, the Fluoride doped tin oxide (FTO) was used as working electrode. It has been exposed in the chemical bath to deposit CdO thin films an area 0.50 cm^2 and resistance 15 ohm/cm^2. Prior to electro deposition, the FTO substrates were cleaned ultrasonically for 5 minutes in acetone and ethanol. The etching process was carried out for 2 minutes in diluted nitric acid and finally washed with deionized water. Platinum and Ag/AgCl were employed as counter and reference electrode respectively. During deposition process, -0.7V potential voltage is maintained with respect to Ag/AgCl and a scan rate 20mV/s. The deposition time of all samples was fixed for 20 minutes.

Finally, the effect of bath temperature and supporting electrolyte were analyzed in prepared samples by X-ray diffraction (XPERT-PRO, 1.540A□), photoluminescence spectrometer (Cary eclipse metry, xenon lamp 150 watt) and Scanning Electron Microscope (HITACHI-3000N).

Results and Discussion

1. Structural studies

Figure 1 shows the X-ray diffraction patterns of $Cd(OH)_2$ and CdO thin films synthesized at bath temperature of 30ºC and 70ºC. All thediffraction peaks of as prepared thin films are corresponding to the lattice plane of $Cd(OH)_2$(001), (100),(101), (002), (102), (111), and (112) respectively (JCPDF card number: 31-0228). The small weak reflection appeared at 34.10˚. Which is belongs to hkl plane (111) of cubic CdO thin films. Further, increasing bath temperature 70˚ C, the predominate plane (001) had vanished whereas the plane at(111) only persisted, when the bath temperature increases, the$Cd(OH)_2$ converted intoCdO. The crystalline size, dislocation density and micro strain for as-prepared CdO thin films are calculated and are tabled in table.1 [12, 13].

Table .1the crystalline size, Dislocation density and strain of as-synthesized thin films.

Sample	Bath temperature (˚C)	Crystalline size D (nm)	Dislocation density X10^{14} (lines/m^2)	Strain X 10^{-3} ($line^{-2}.m^{-4}$)
A	30	67	2.21	0.08
B	70	27	13	0.38

1.1 Structural studies

XRD pattern of the CdO thin film annealed at 350˚Cis shown in Fig.2, in whichthe hexagonal $(OH)_2$ converted into cubic CdO thin film after annealing the sample. All the peaks in the pattern closely coincided with JCPDS card number 75-0591. The X- ray diffraction peaks at 2θ = 33.44, 38.72, 55.72, 66.29 and 69.24˚ has indexed(111), (200), (220), (311) and (222) is formation of polycrystalline CdO. The predominant peak at (111) plane indicates their axial growth direction. It has been observedthat the crystalline size decreases after annealing the as prepared sample. This may be removal of hydroxide from cadmium hydroxide ($Cd(OH)_2$). During film deposition and post-deposition treatments, there is always a possibility for developing some strain (stress) in the films. Strain affects the mechanical properties of the films such as the stability of microstructure and the adhesion between film and substrate. Strain in the films is to be intrinsic, caused by the condition prevailing during deposition. The observed (200) orientation growth in CdO films prepared by different techniques is enhanced by post-annealing [13,14].

Table 2 the crystalline size, Dislocation density and strain for annealed samples.

Samples	Bath temperature (˚C)	Crystalline size D (nm)	Dislocation density X10^{14} (lines/m^2)	Strain X 10^{-3} ($line^{-2}.m^{-4}$)
A	30	21.27	22.09	0.48
B	70	27.65	13.07	0.37
C	70	75.45	1.75	0.13

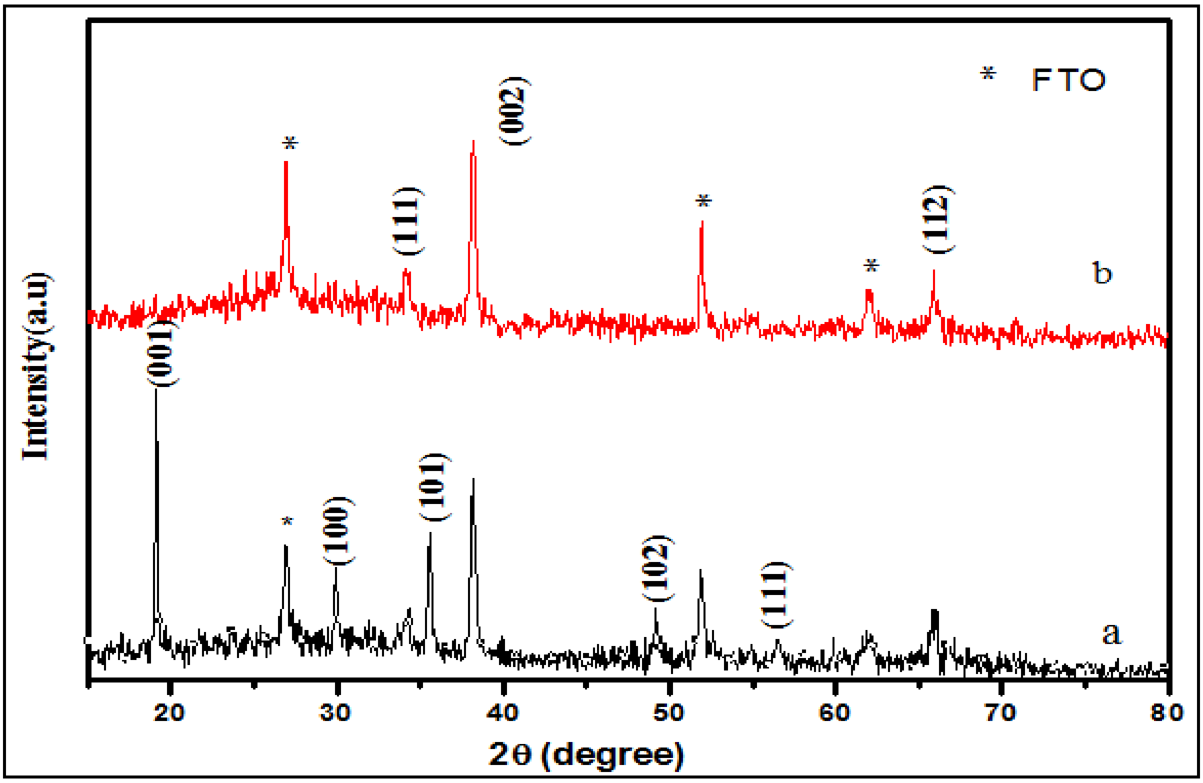

Figure .1 XRD pattern of as-prepared $Cd(OH)_2$ and CdO thin film synthesized in different bath temperature. (a).30˚ C, (b). 70˚C.

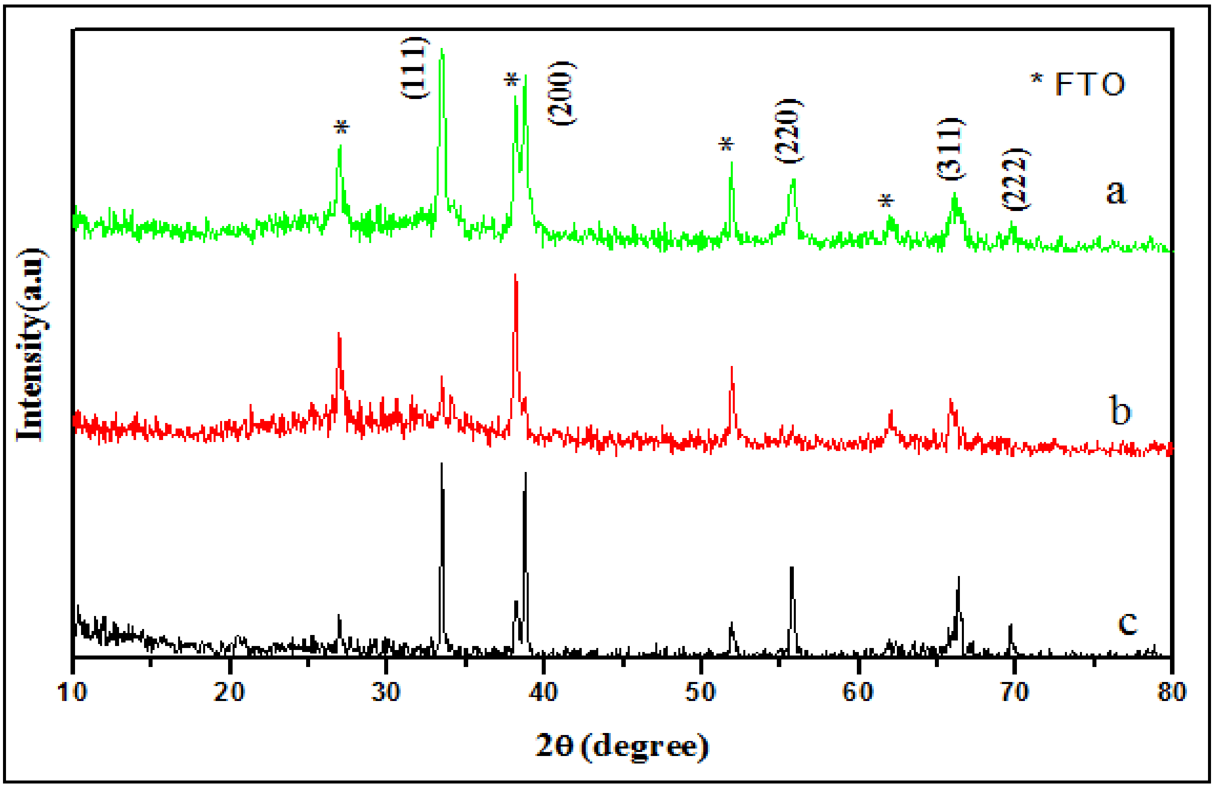

Figure 2 XRD pattern of annealed CdO thin film at different bath temperature. (a) 30˚ C, (b)70˚C and (c)70 ˚C with KCl

Optical studies

Room temperature photoluminescence (PL) emission spectra were carried out at an excitation wavelength 250 nm for three CdO thin films prepared by electrochemical deposition. Those spectra are shown in figure 3. There are three emission peak obtained all the samples. The weak peak appeared at 395 nm (3.13

eV) are attributed to transition between states at the bottom of the conduction band and the top of the valence band of the CdO thin film and band edge emission [15,16] . The strong emission peaks centered at 420 nm (2.96 eV) are assigned due to an exciton bound to a donor level[17]. The other wide peaks at 460 nm are located in the visible spectrum at approximately 2.6 eV and are associated with emission due to impurity levels. Thedefect-related luminescence peak is obtained with broad band due to radiative transitions between oxygen vacancies. In other hand, it may havebeenraisedCd interstitials acting as shallow donors and Cd vacancies acting as deep acceptors. Which leads to the recombination mechanism and competes with excition-related luminescence depend on the stoichiometry and the preparation conditions (such as bath temperature, concentration and pH) of the CdO thin films[18].

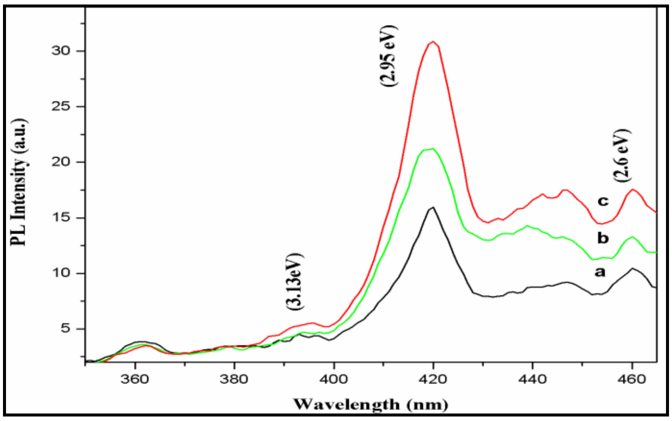

Figure (3) Annealed PL spectra of CdO thin film at different bath temperature: (a).30˚C, (b). 70˚C, (c).70 ˚C with KCl.

Morphological Studies

The electrical and optical properties in the application of optoelectronic devices are very important factors with respect to surface properties of transparent conducting oxide thin films. Suppose, surface roughness of the prepared sample increases which leads to enhance the propagation loss in surface acoustic wave devices (SAW) and simultaneously the efficiency is also reduced for the photovoltaic solar cell. In the present study, the surface morphology of the annealed CdO films at 350˚C was studied using SEM analysis and is shown Fig.4. The surface properties of the annealed sample prepared at 30˚C bath temperature shows crack in microstructures and more roughness as shown in Fig. 4(a). In other hand, Fig. 4(b) shows the SEM micrograph of CdO thin film synthesized at 70˚C bath temperature. It can be clearly visualized from SEM micrographs that the film has a smooth and a homogeneous surface morphology and particles are distributed over the surface as temperature to 70˚C. Trilok Sing et al., obtained this kind of particle structure on varying annealing temperature [19]. In the figure 4(c), SEM image is shown a smoothness and big agglomerated particle than sample 4(b) due to thesupporting electrolyte 0.1M of KCl is added at bath temperature 70˚C.

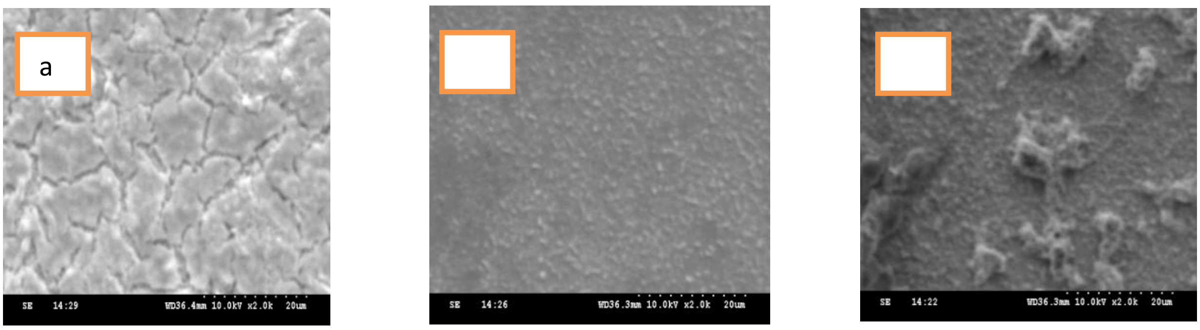

Fig 4 SEM image for annealed CdO thin film in bath temperature: (a) 30˚C, (b) 70˚Cand (c) 70˚C with KCl.

Conclusion

In the present work CdO thin film on FTO substrate has been successfully deposited by electrodeposition technique. The crystal structure of deposited film was analyzed by X-ray diffraction analysis revealed that, the deposition films were to be polycrystalline in nature with cubic structure. It is observed that when the bath temperature increases the quality of the film is good. The height of predominant peak and orientation of the crystallites are found to be depending upon the bath temperature. The optical characteristic of the deposited films were analyzed using photoluminescence spectra. It is observed that room temperature photoluminescence spectrum exhibited a UV emission band at 395 nm. The bath temperature at 70 □C photoluminescence exhibited a UV emission band at 420 nm. The surface morphology of the deposited films was analyzed using SEM. It is observed that the film deposited at low bath temperature have more crack and roughness whereas the films deposited at high bath temperature have smooth and homogenous morphological textures.

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