

Influence of Deposition Time on the Microstructure and Transport Properties of CdO Thin Films Prepared by Chemical Bath Deposition

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ABSTRACT

Transparent thin films of CdO has been deposited on to glass substrates employing chemical bath deposition. The prepared films are reproducible, adherent to the substrate, pinhole free and uniform. Amongst the different process parameters, the deposition time plays a significant role in obtaining device quality transparent CdO thin films. X-ray powder diffraction (XRD) studies indicated that the thin films are polycrystalline in nature with cubic phase with a cell constant of $a = 4.638 \text{ \AA}$. The surface morphology of the prepared CdO thin films was examined by scanning electron microscopy. The films deposited at 24 hrs exhibited highest optical transmittivity (>80%) and the direct band gap energy was found to vary from 2.50 to 2.91 eV with a rise deposition time from 6 to 30 hrs. The electrical resistivity variations of these films were measured in the temperature range between 30°C and 150°C by four-probe technique.

Keywords: Cadmium Oxide; Chemical Bath Deposition; Transparent Electrode

1. Introduction

Thin films of transparent conducting oxides (TCO) such as doped metal oxide thin films like zinc oxide, indium oxide, tin oxide and cadmium oxide have attracted considerable attention because of their low resistivity and high optical transmittance [1-4]. They are widely used for many applications such as flat panel display, light emitting diodes and photovoltaic cells [5-7]. Among these TCO, cadmium oxide (CdO) has received considerable attention for solar cell application due to its low electrical resistivity and high transparency in the visible range of solar spectrum [8]. Different techniques such as sol-gel [9], DC magnetron sputtering [10], radiofrequency sputtering [11], spray pyrolysis [4], chemical vapor deposition [12], chemical bath deposition [13], and pulsed laser deposition [14] have been used to deposit CdO thin films.

Literature survey confirmed that there are only few reports on the chemical synthesis (also known as chemical bath deposition, CBD) of CdO thin films [15]. Chemical bath deposition, which has been well known as prevalent low temperature aqueous method for directly depositing large-area thin films of semiconductors has advanced

over above-mentioned techniques because it allows films to be deposited on nonplanar substrates that might not be chemically or mechanically stable at high temperatures [16]. Moreover, it requires no sophisticated instruments such as vacuum systems, etc., and the starting chemicals are commonly available and cheap. Also, the preparative parameters are easily controlled. The principles of direct deposition of film via CBD method is based on a gradual release of metal ions from super saturation solution. A chelating agent is usually used to limit the hydrolysis of the metal ion and impart some stability to the bath, which would otherwise undergo rapid hydrolysis and precipitation. It is well known that there are distinct mechanisms or models leading to the formation of CBD films, notably: 1) adsorption and coagulation of colloids performed solution by homogeneous reaction (as usually called cluster-by-cluster process), and 2) ion-by-ion condensation at the surface of the substrate by heterogeneous reaction. In practice, both processes may occur and/or interact in the growing films. The predominance of one mechanism over another is controlled by the extent of heterogeneous and homogeneous nucleations. Key parameters include the degree of supersaturation of the solution and the catalytic activity of the sur-

face of the substrate. Many metal chalcogenide [17] thin films have been deposited by CBD, however, only a few oxide including NiO, TiO₂, ZnO and MnO thin films have been deposited via this technique [16,18-21]. Our main interest is to prepare CdO thin films by using chemical bath deposition method, which is applicable for gas sensing applications. In this work, we report on the structure, morphology, optical, and electrical properties of CdO thin films prepared by CBD method. The films were deposited onto glass substrate. Different deposition parameters like deposition time is optimized to get pin hole free adherent CdO thin films at room temperature.

2. Methodology

The cadmium oxide films were prepared on to pre-cleaned microscopic glass substrate. Prior to film coating, the substrate was cleaned in soap solution, hot chromic acid solution, rinsed with double distilled water, and dried in air, in order to achieve a better adherence between the film and the substrate. The substrates were finally cleaned with acetone before use. The CdO thin film was grown on glass substrate by a chemical bath deposition method using cadmium chloride (0.1 M) as a Cd²⁺ ion source. For the complex formation, an excess ammonium hydroxide solution was added (30%) to get clear solution. This clear solution was kept under unstirred condition and glass substrate was dipped vertically various times like for 24, 36 and 48 hrs respectively. Whitish films due to the Cd(OH)₂ were formed on glass substrate. The CdO films were heat treated in oxygen air-tight container at 623 K for 2 hrs which generally facilitates decrease in dislocations, stresses, and inhomogeneities. The whitish films were found to be turning to brownish during the formation of CdO.

The crystalline structure of the prepared films calcinated at 623 K for 2 hrs was investigated by X-ray diffraction using X³ pert PRO (PANalytical) diffractometer with CuK α radiation ($\lambda = 0.15405$ nm) and employing a scanning rate of 5 min⁻¹ over a range of 10° - 70° at the room temperature. The morphological characteristics of the thin film after calcination was examined by scanning electron microscope (Philips Model XL 30), In order to determine the band gap energy of the films, optical transmission study was carried out in the wavelength range 350 - 950 nm, using Perkin Elmer Lambda 35 spectrophotometer. The electrical resistivity of the films is studied by four-probe technique.

The film thickness was determined by the weight gain method using the formula.

$$t = \frac{m}{A\rho} \quad (1)$$

where “*t*” is the thickness of the film, “*m*” is the weight gain; *A* is the area of the coated film and ρ is the density

of the film (8.15 gm/cm³). The film thickness was estimated and given in **Table 1**.

3. Results and Discussions

Figure 1(a)-(c) shows the typical X-ray diffractograms of CdO thin films prepared with different deposition time. The prepared CdO thin films were showed an increase in crystallinity with increase in the deposition time. The crystals showed those XRD reflections that correspond very well with NaCl structure of CdO [22]. It also indicates the presence of (111), (200), (220), (311) and (222) planes for cubic CdO. Similar results have been observed by Zhao *et al.* [23], by chemical vapor deposition and Mane *et al.* [24], by layer-by-layer deposition. The lattice parameter “*a*” is calculated for cubic structure of CdO. The calculated lattice constants are shown in **Table 1**, which is in good agreement with standard “*a*” value [25]. The surface morphological image of CdO thin films was observed by scanning electron microscope. **Figures 2(a)-(c)** reveal the different surface layer of CdO thin films prepared at deposition time 24, 36 and 48 hrs. The SEM photograph shows uniform and homogeneous distribution of crystalline nature. In addition to the above, the surface morphology of the cadmium oxide films shows an increase in grain size with increasing deposition time. EDAX spectrums were taken for CdO thin films prepared at 48 hrs. The observed peaks are shown in **Figure 2(d)** and it shows that the sample contains Cd,

Table 1. Film thickness, crstallite size and lattice constants of CdO thin films prepared at deposition time 24, 36 and 48 hrs.

Preparation condition	Parameters	<i>t</i> (μ m)	<i>P</i> (nm)	Lattice constant <i>a</i> (nm)
Deposition time	24 hrs	0.77	49	4.691
	36 hrs	0.91	62	4.635
	48 hrs	1.25	74	4.654

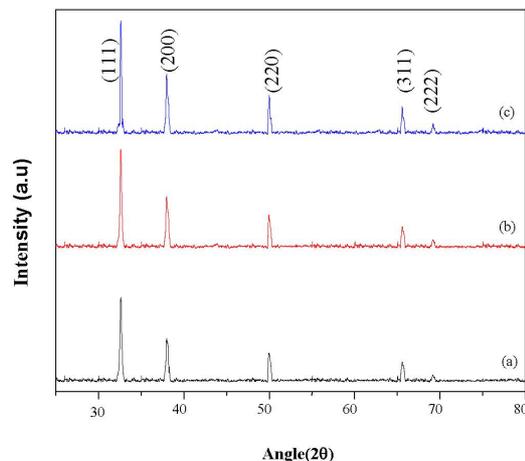


Figure 1. (a)-(c) X-ray diffraction pattern of CdO thin films prepared at deposition time 24, 36, and 48 hrs.

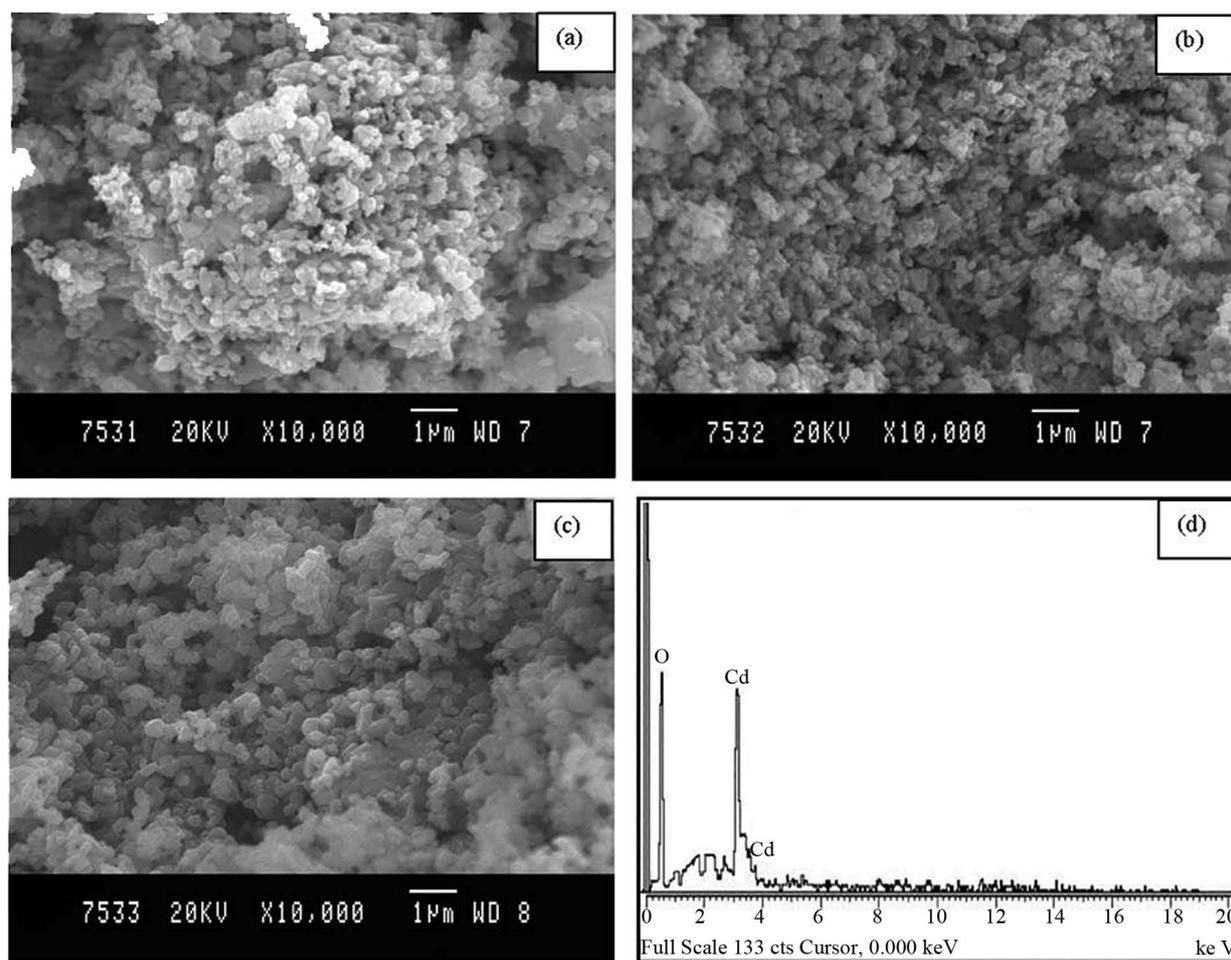


Figure 2. (a)-(c) SEM images of CdO thin films prepared at 24, 36 and 48 h. (d) EDAX spectrum of CdO thin films prepared at 48 hrs.

O elements without any impurities. The variation of optical transmittance (T) with wavelength (λ) of CdO thin films is shown in **Figure 3(A)**. This spectrum reveals that the as prepared CdO thin films have high transmittance in the visible region. The increase in transmittance values are 87%, 92%, 89% for the film prepared at deposition time 24, 36 and 48 hrs. This indicates that the absorption band gap transitions in the studied crystals are due to direct transition, which is characteristic of CdO film. The fundamental transmission, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the nature and value of the optical band gap. The relation between the absorption coefficient (α) and the incident photon energy ($h\nu$) can be written as,

$$A h\nu = \alpha_0 (h\nu - E_g)^n \quad (2)$$

where α_0 is a constant, $h\nu$ is the photon energy, E_g is the band gap of the material and the exponent n depends on

the type of transition. $n = 1/2, 2, 3/2,$ and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. In **Figure 3(B)** taking $n = 1/2,$ and $n = 2,$ $(\alpha h\nu)^2$ vs. $h\nu$ graph was plotted and extrapolating the linear portion of the graph to the “y” axis allowed direct band gap was determined from the intercepts. Those values found to be 2.85 eV, 2.81 eV and 2.75 for films prepared for the deposition time 24, 36 and 48 hrs respectively. These energies are slightly higher than earlier reported by Dakhel and Henari [26] and Gurumurugan *et al.* [27] and slightly smaller than earlier reported by Carballedda-Galicia *et al.* [28] and Gurumurugan *et al.* [29].

Figure 4(a)-(c) shows the variation of $\log \rho$ versus $1000/T$ for CdO thin films prepared at deposition time 24, 36 and 48 hrs. For all the samples it is observed that the resistivity decreases with increase in temperature, confirming the semiconducting nature of the films. The activation energy values E_a are calculated by using the relation

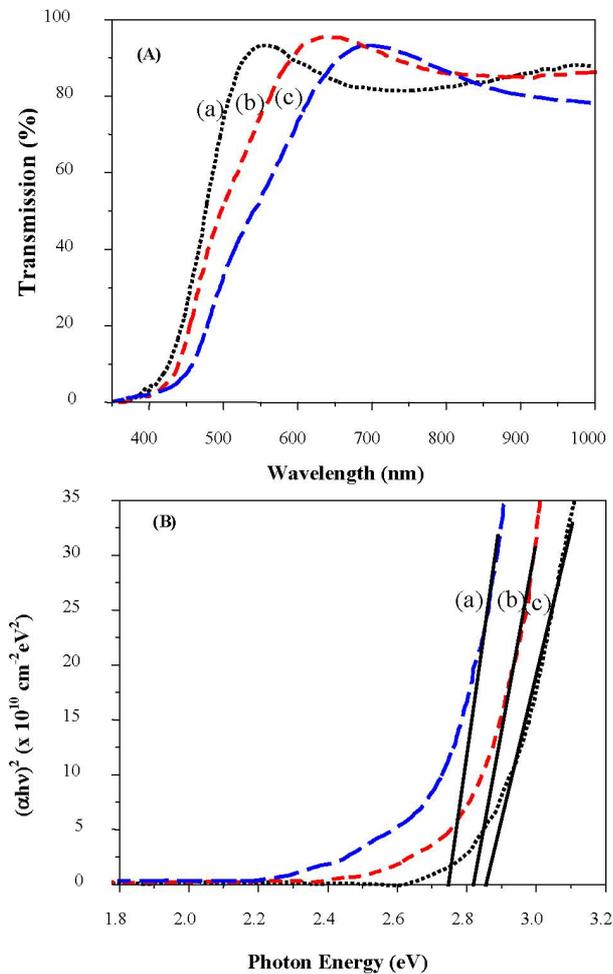


Figure 3. (A) Transmission spectrum and (B) Band gap of CdO thin films prepared at deposition time 24, 36 and 48 hrs.

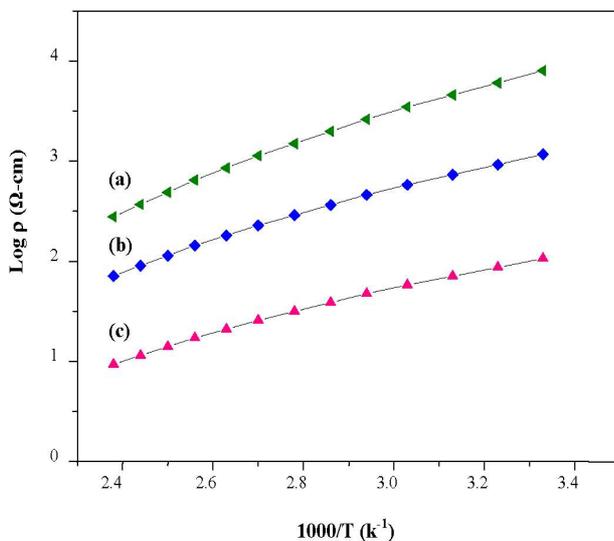


Figure 4. (a)-(c) Variation of log ρ versus 1000/T for CdO thin films prepared at deposition time 24, 36 and 48 hrs.

$$\rho = \rho_0 \exp\left(\frac{-E_a}{kT}\right) \quad (3)$$

where “ ρ_0 ” is a constant, “ k ” the Boltzmann constant and “ T ” the temperature in Kelvin. The values of activation energy E_a are 0.38, 0.31, and 0.24 for deposition time 24, 36 and 48 hrs respectively. It is observed that activation energy decreases with increase in deposition time.

4. Conclusion

Influence of deposition time in the CBD grown CdO thin film was investigated. The present method is simple, economic and easily reproducible for producing low cost cadmium oxide nanowires. XRD studies revealed the formation of polycrystalline cubic CdO thin films at all deposition times and the crystallinity was found to increase with increasing time. The lattice constants are reported. The optical transmittance measurement showed that the films exhibit smooth surface, with average transmittance over 80% in the visible region. The band gap of the films showed a decrease in the value with deposition time. The values of band gap are 2.85, 2.81 and 2.75 eV for films prepared with deposition time 24, 36 and 48 hrs respectively. Electrical studies revealed that the resistivity decreases with increase in temperature, confirming the semiconducting nature of the films. The activation energies were estimated and reported.

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