

An Investigation of SILAR Grown CdO Thin Films

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ABSTRACT: Cadmium oxide (CdO) thin films were deposited on the glass substrate by the modified SILAR method, using cadmium acetate dihydrate and ammonium hydroxide aqueous solution as precursors. The structural, surface morphological, elemental composition and optical properties of the deposited films were investigated via X-Ray Diffraction (XRD), scanning electron microscopy, EDAX, optical absorption, photo luminescence and FT-IR spectroscopy. The XRD analysis reveals that the films were polycrystalline with cubic structure. Both crystallinity and grain size were found to increase with increasing solution concentration. The energy-dispersive spectroscopic analysis confirmed the presence of Cd and O elements. The films exhibited a maximum transmittance (50% - 70%) in the infra-red region. Transmittance was found to increase with increasing precursor concentration and estimated band gap energy (E_g) was in the range of 2.17 – 2.21 eV.

KEYWORDS: CdO; Thin films; XRD; SILAR; Optical studies.

INTRODUCTION

Transparent Conducting Oxide (TCO) films have high technological applications in the field of optoelectronic and other solid state devices [1]. The various oxides of SnO₂, ZnO, InO₂, ITO, FTO and CdO are used as transparent electrodes in solar cells and other electronic components [2]. CdO is one other promising transparent conducting oxide from II-VI group of semiconductors having high absorbance and emission capacity of radiation in the energy gap [3]. In recent, years researchers have focused on CdO due to its applications, especially in the field of optoelectronic devices such as

solar cells [4, 5]. However, many of their physical properties were found to be depending on the methods and conditions of preparation [6]. A variety of techniques such as DC magnetron reactive sputtering [7], Metal-Organic Chemical Vapor Deposition (MOCVD) [8,9], vacuum evaporation [10], electrochemical deposition [11], Pulsed Laser Deposition (PLD) [12], spray pyrolysis [13], electron beam evaporation [14], Chemical Vapor Deposition (CVD) [15], sol-gel technique [16], Chemical Bath Deposition (CBD) [17,18] and Successive Ionic Layer Adsorption and Reaction (SILAR) [19] technique

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have already been employed to prepare CdO thin films. Among these deposition techniques, SILAR has many advantages such as low cost, simplicity, and reproducibility. Moreover, anion and cation precursor in different baths offers good control over the deposition parameters such as pH, deposition temperature and time, etc. The only disadvantage of this technique is the formation of the hydroxide phase while oxide growth and slow growth rate [20]. In this work, CdO thin films were prepared by SILAR method and the structural, optical and transport properties of the CdO thin films are discussed in detail.

EXPERIMENTAL SECTION

Synthesis of CdO thin films

In the present work, CdO thin films were prepared on a glass substrate by the modified SILAR method. This method consists of two beaker system. Before deposition, the glass substrates were cleaned in hot chromic acid followed by rinsing in distilled water and cleaning with alkali and acetone. CdO thin films were prepared using a SILAR technique involving double dip. CdO thin films were grown using a two-step modified SILAR using a solution comprising cadmium acetate dihydrate [$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] (99% e-Merck) with different molarities (0.05 M and 0.1M) and ammonium hydroxide with a pH value of 7 ± 0.2 deposited at bath temperature of 90°C under optimized condition. The complexing agent ammonium hydroxide was used to stabilize the crystallite size [21, 22]. In normal SILAR, four beakers were used. Anionic and cationic precursor solutions are taken in separate beakers. But in a modified SILAR all the precursor solutions are taken in a single beaker [23]. The main advantages of two beakers SILAR system is reducing the work and time. The well-cleaned substrates were immersed in the chemical bath for 20 seconds and followed by immersion in hot water at the same time for hydrogenation. The process of solution dip (step 1) followed by hot water dipping (vary step 2) is repeated for 20 dipping cycles. The cleaned substrate was alternatively dipped for a predetermined period in cadmium ammonium bath and water bath kept at room temperature and near boiling point, respectively. After 20 dipping cycles, the whitish thin films were formed on a glass substrate. The coated films were dried in air and annealed at a temperature of 200°C for 1 hour. After annealing the whitish films were found to be turning to brownish during the formation of CdO.

Characterization Studies

The thickness of the coated films was measured using the weight gain method using the formula [24].

$$t = m / (A\rho) \quad (1)$$

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. The film thickness increased with the increase of solution molar concentration. The film thickness was estimated to be approximately 410 nm and 424 nm for the molar concentration of 0.05 M and 0.1 M respectively.

The CdO thin film formed was confirmed by XRD (Rigaku Ultima III) analysis and the micro structural analysis of the samples was performed using SEM (JEOL Model JSM - 6390LV). The optical properties were estimated by transmittance and absorption measurements using a UV-Vis NIR spectrophotometer (PerkinElmer UV WinLab 6.0.3.0730). Infrared absorption spectra were recorded at room temperature using a Fourier transform interferometer (model Bruker IFS113v) in the range of 400 cm^{-1} to 4000 cm^{-1} . The room temperature PL measurements were carried out by using the Xe lamp with an excitation wavelength of 360 nm.

RESULTS AND DISCUSSION

Structural Studies

Fig. 1 (a-b) shows the X-ray diffraction pattern of the CdO thin films deposited with 0.05 M and 0.1 M solution concentrations. The presence of three peaks (111), (200) and (311) indicates the polycrystalline with the cubic structure of the films. All the diffraction peaks of XRD pattern could be indexed to the cubic crystal structure of CdO, which is in good agreement with the standard data for CdO (JCPDS data file no. 78-0653). This is in accordance with the reports on CdO thin films prepared by SILAR method. In the present investigation, the films exhibit a preferential orientation along with the (111) diffraction plan.

The crystallite size D has been calculated from the Scherer formula [15, 25]

$$D = (k\lambda) / (\beta \cos \theta) \quad (2)$$

Where k is the shaping factor which takes value from 0.89 to 0.94, λ is the wavelength of the $\text{Cu-K}\alpha$ line, β is the Full Width at Half Maxima (FWHM) in radians and

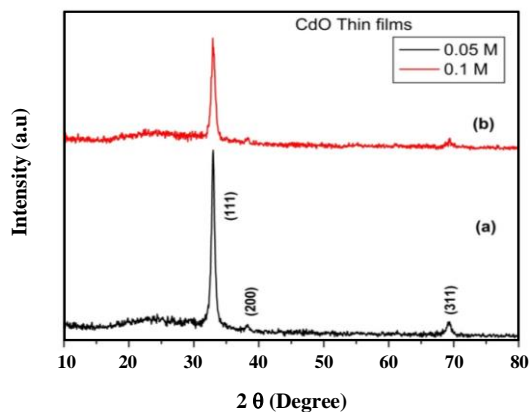


Fig. 1: XRD pattern of CdO Thin films (a) 0.05 M and (b) 0.1 M

' θ ' is the corresponding Bragg's angle. The crystalline size was found to be in the nano range (24.05 – 42.09 nm) as the solution concentration increases from 0.05 M to 0.1 M. With the increase in solution concentration, the FWHM and 2θ values are decreases, thus apparently shows an increase in the size of the crystallites. These results are confirmed by the SEM image (Fig. 2).

Dislocation density (δ) for (111) plane is evaluated using the relation [26]

$$\delta = 1/D^2 \quad (3)$$

The lesser value of (δ) obtained (5.643×10^{14} lines/m²) for coated with 0.1 M indicated that the degree of crystallization is higher for the films with higher molarity. The strain (ϵ) is calculated from the following relation

$$\epsilon = (\beta \cos \theta) / 4 \quad (4)$$

The number of crystallites (N_c) per unit area was calculated using this relation [27]

$$N_c = t / D^3 \quad (5)$$

Where t is the thickness of the film. Observed and standard more interplane distances with calculated structural parameters are shown in Table 1. It is seen from the table, dislocation density and strain decreases, whereas grain size increases, which indicates the improvement in the crystallinity. This improvement can be attributed to the enhancement of clusters and removal of the defects formed during the thin film deposition.

SEM and EDAX Studies

Fig. 2 (a-b) shows the SEM micrographs of the surface of CdO films prepared with 0.05 M and 0.1 M of cadmium acetate. The film prepared with 0.05 M of solution concentration has small grains of size distributed throughout the surface. It is also seen there is the overlapping of a large number of small spherical grains, which are aggregated together from resistively big islands. However, films coated with 0.1 M shows uniform distribution of grains with size larger than the size coated 0.05 M. It is observed that the grain size increases with molarity which is evident for the XRD results.

The elemental composition of the deposited 0.05 M and 0.1 M solution concentration of CdO thin films was investigated using EDAX pattern is shown in Fig. 2 (c-d). Peaks Cd and O exhibit the presence of these elements in the prepared films. The peaks of silicon and oxygen originate from the glass substrate. It is possible in SILAR deposited thin films may be contaminated with oxygen from the environment as the film is exposed to the environment during deposition.

Optical Studies

Fig. 3 shows the optical transmission spectra of CdO thin films deposited with 0.05 M and 0.1 M aqueous solution of cadmium acetate. The maximum transmittance values obtained in the wavelength range 350 nm to 1100 nm was found to be 55% and 80% for the films coated with 0.1 M and 0.05 M respectively. Because a high concentration solution has more atoms compared to less concentration solution. Maximum atoms are absorbed in the film prepared with 0.1 M solution. So the fewer transmittance values are observed. The spectra of all the films show a sharp fall in transmission near the fundamental absorption, which is an identification of the good crystallinity of these films. Also a shift of the absorption tail towards long wavelengths is observed.

The fundamental absorption, which corresponds the transition from valance to conduction band, can be used to determine the optical band gap energy of the material. The absorption coefficient (α) can be calculated from the transmittance (T) values from the Lambert law.

$$\left[\alpha = \frac{\ln(1/T)}{t} \right] \quad (6)$$

The variation of absorption coefficient with photon energy ($h\nu$) takes the form, where E_g is the band gap,

Table 1: Structural parameters of CdO Thin films

Cadmium acetate Molar concentration	d lattice spacing		Thickness (nm)	Grain size (D) × 10 ⁻⁹	Dislocation density (δ) × 10 ¹⁴ /lines/ m ²	Strain (ε) × 10 ⁻³	Number of crystallite per unit area (N _c) × 10 ⁻¹⁵
	observed (A ⁰)	calculated (A ⁰)					
0.05 M	2.71417	2.71203	410	24.05	17.277	2.255	29.4451
0.1 M	2.72003	2.71778	424	42.09	5.643	1.291	5.6848

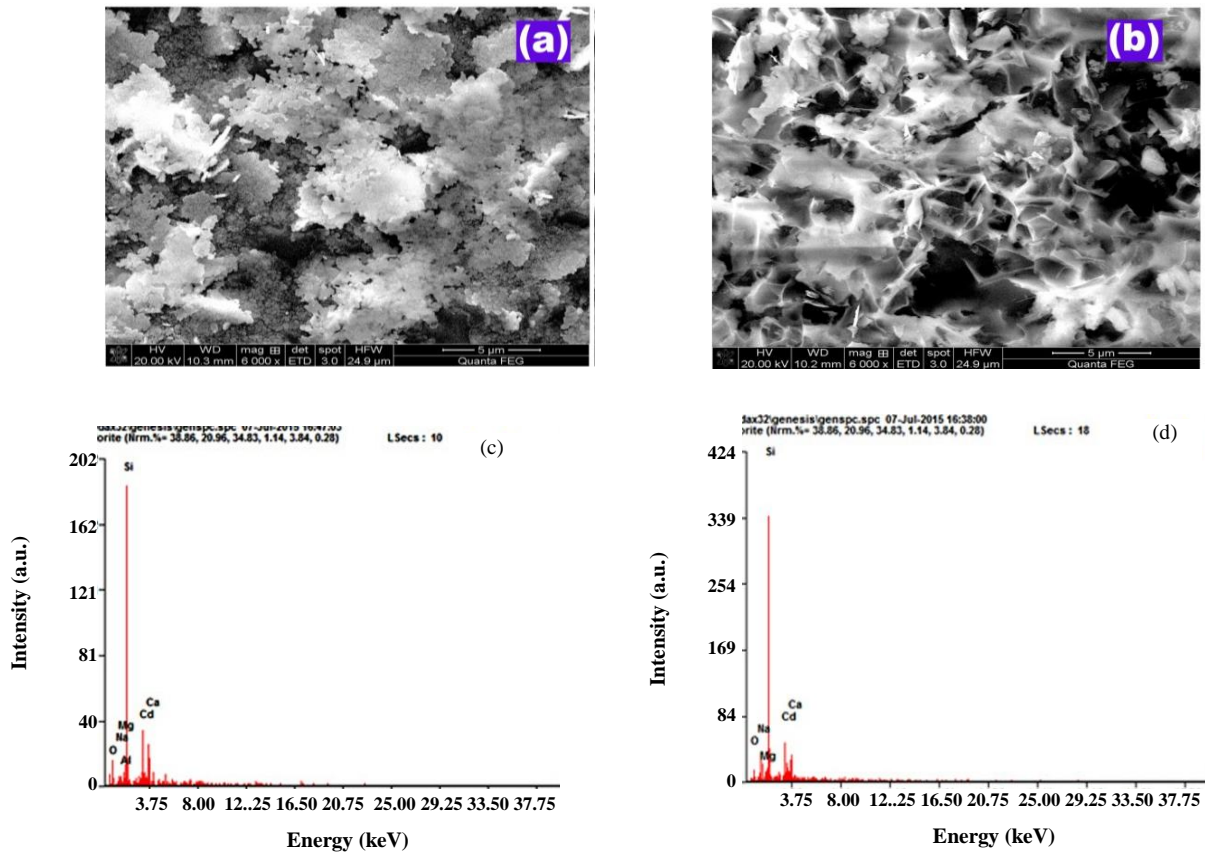


Fig. 2: SEM and EDAX of CdO Thin films.

A is a constant related to the effective masses associated with the bands and n is a constant which is equal to one for a direct-gap material and four for an indirect-gap material. To decide whether the CdO films have a direct or indirect band gap, $(ah\nu)^2$ vs. $(h\nu)$ and $(ah\nu)^{1/2}$ vs. $(h\nu)$ plots are drawn. Since better linearity is obtained in the $(ah\nu)^2$ vs. $(h\nu)$ plot, the direct band gap values are determined by extrapolating the linear portion of this plot to the energy axis (Fig. 4).

$$\alpha = A(h\nu - E_g)^{n/2} \quad (7)$$

The variation in a solution concentration of deposited CdO showed the energy band gap of CdO film increases

with an increase in concentration. The band gap values obtained for the prepared CdO films were found to be 2.17 eV and 2.21 eV for 0.05 M and 0.1 M solution concentrations respectively. These values are good agreement with the values reported by others [28]. The uniform increase in absorbance and energy band gap value represents the formation of optically active CdO thin films.

Photoluminescence Studies

Room temperature photoluminescence (PL) emission spectra were carried out at an excitation wavelength of 360 nm for 0.05 M and 0.1 M coated CdO thin films prepared

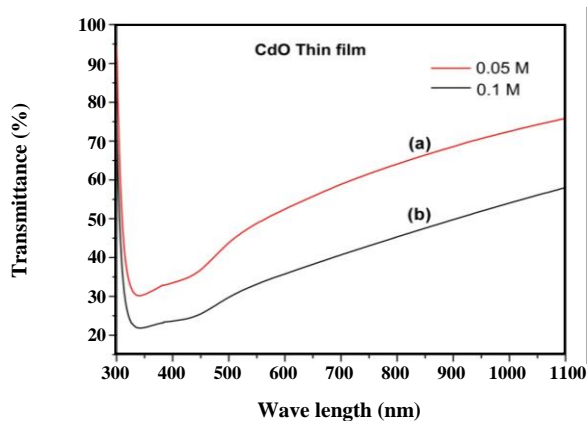


Fig. 3: Transmittance spectra of CdO thin films.

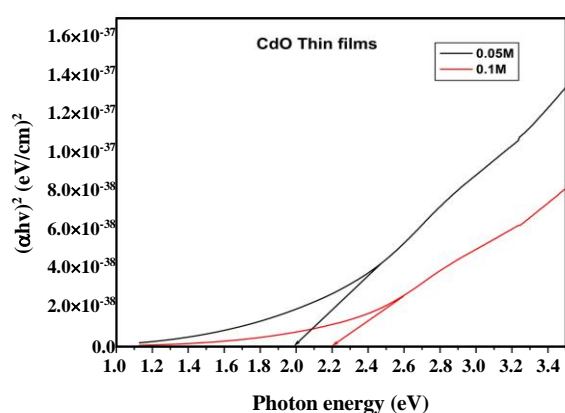


Fig. 4: Optical band gap variations of CdO thin films.

by the modified SILAR method. Those spectra are shown in Fig. 5. There are three emission peak obtained all the samples. The weak peak appeared at 554 nm (2.23 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 [29, 30]. The strong emission peaks centered at 569 nm (2.17 eV) are assigned due to an exciton bound to a donor level [31]. The other peaks at 583 nm are located in the visible spectrum at approximately 2.12 eV and are associated with emission due to impurity levels. The defect-related luminescence peak is obtained with broad bands due to radioactive transitions between oxygen vacancies. On the other hand, it may have been raised Cd interstitials acting as shallow donors and Cd vacancies acting as deep acceptors. This leads to the recombination mechanism and competes with exciton-related luminescence depend on the stoichiometry and the preparation conditions (such

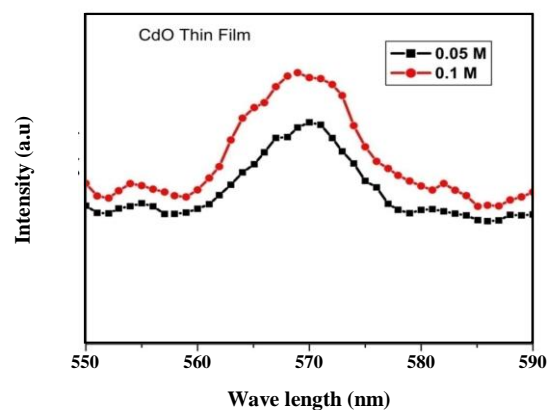


Fig. 5: PL spectra of CdO thin films.

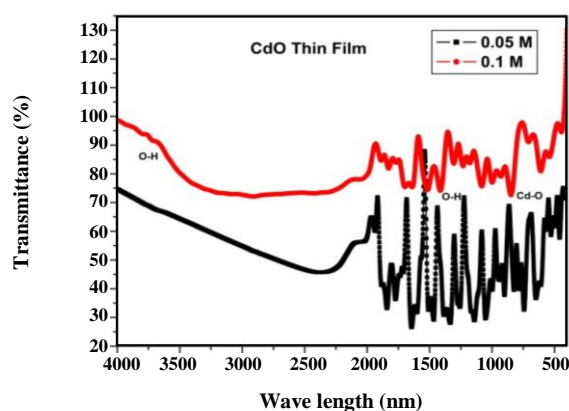


Fig. 6: FT-IR spectra of CdO thin films.

as bath temperature, concentration and pH) of the CdO thin films [32].

FT-IR Studies

FT-IR analysis was carried out to understand the role of metal ion during synthesis and annealing as illustrated in the corresponding spectra as shown in Fig. 6. The peaks observed at around 460.25 cm^{-1} and 878 cm^{-1} correspond to the formation of symmetric and asymmetric vibration frequencies of Cd and O bond. These bands become stronger on increase the molar concentration, supporting the formation of a strong Cd–O–Cd frame-work after the removal of surface impurities. The appearance of the absorption band at 719.37 cm^{-1} supports the formation of Cd–O phase. The peaks at 3437 cm^{-1} and 1436.47 cm^{-1} occur due to the vibration and deformation frequency of OH group which occurs due to the absorption of water during sample preparation [33].

Table 2. Optical band gap values of CdO Thin films.

CdO Molar concentration	Optical band gap value (eV)	
	From UV (eV)	From PL (eV)
0.05 M	2.17	2.17
0.1 M	2.21	2.18

CONCLUSIONS

Transparent conducting cadmium oxide thin films were prepared by cost effective modified SILAR method. XRD studies show that all the films are polycrystalline in nature with cubic structure having preferential orientation along (111) plane. Microstructural parameters have been calculated for prepared samples. Crystallite size increases from 24.05 nm to 42.09 nm as the solution concentration increases. The optical transmittance in the visible range is greater than 75%. The optical band gap of the coated CdO films increases with the increase in solution concentration. The films were found to be good physical properties desirable for solar cells and other opto – electronic applications.

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