Chapter 3

Preparation and Characterization of Cadmium Oxide Thin Film as a Transparent Conducting Electrode

3.1. Introduction

Transparent conducting oxides (TCOs) have generated great fundamental and technical interest in recent years [1, 2]. It is due to their exceptional combination of high electrical conductivity ($> 10^3 \, \Omega^{-1} \, \text{cm}^{-1}$) and good optical transparency in the visible region of the spectrum. TCOs have been used in several fields such as flat panel displays, photovoltaic cells, low emissivity windows, electrochromic devices, chemical/biological sensors and transparent electronics [3, 4]. Current materials are based on n-type metal oxide thin films which include tin-doped indium oxide In$_2$O$_3$: Sn (ITO), fluorine doped tin oxide SnO$_2$: F (FTO), aluminum doped zinc oxide ZnO: Al (AZO), gallium oxide (Ga$_2$O$_3$), cadmium oxide (CdO) etc [5, 6]. Badeker first observed in 1907 that an evaporated film of cadmium metal oxidized in air becomes transparent without compromising its electrical properties. Although, CdO was the first to be reported as a transparent conducting oxide, but due to its relatively low intrinsic band gap 2.4 eV it has not been studied extensively [7, 8].

At present, tin-doped indium oxide (ITO), with a typical electrical conductivity of 3-5 x10$^3$ S/cm and 85-90% transparency in the visible region, is employed on a huge scale as a transparent electrode in many display technologies. However, there are several drawbacks that cloud its future applicability: (a) the limited availability and high cost of indium; (b) the relatively low conductivity (not
suitable for large-area displays); (c) significant optical absorption in the blue-green region (not suitable for many full-color displays); and (d) chemical instability in certain device structures (e.g., corrosion in organic light-emitting diode (OLED) devices). The majority of known TCO materials are n-type semiconductors where defects such as oxygen vacancies, impurity substitutions and interstitials donate electrons to the conduction band providing charge carriers for the flow of electric current. In view of these issues, intense research has been focused on understanding fundamental TCO crystal structure-film microstructure-electronic structure-charge transport-optical transparency relationships and on searching for ITO alternatives that are less expensive and possess comparable or higher conductivity and/or wider optical transparency windows. Recently, CdO based TCOs have attracted much of attention among researchers due to its simple cubic crystal structure, relatively large carrier mobility and high electrical conductivity. In addition, Cd$_2$SnO$_4$, CdInO$_4$ and CdO-ZnO thin films have been fabricated with impressive conductivities and good optical transparencies for photovoltaic applications [9, 10].

Rocksalt structured CdO is an n-type degenerate semiconductor which possesses a small indirect band gap ($E_{g \text{ind}}$) of $\sim$0.84 eV and a larger direct band gap ($E_{g \text{dir}}$) of $\sim$2.2 eV. CdO is a highly nonstoichiometric material and generally possesses large carrier concentrations ($\sim$10$^{18}$-10$^{20}$ cm$^{-3}$) together with large electron mobilities in the bulk. These high carrier concentrations generate a pronounced Moss-Burstein (MB) shift which can considerably extend the optical band gap, ($E_{g \text{opt}}$). Donor dopants can extend $E_{g \text{opt}}$ above 3.1 eV, making CdO suitable for TCO applications. Understanding the defect chemistry of CdO is therefore vital for the development of improved TCOs. To date, however, there is still uncertainty regarding the nature of the dominant intrinsic defects in this material. Cd interstitials (Cd$_i$) and oxygen
vacancies ($V_0$) have both been suggested as the dominant defects in CdO. Further, the bandgap of bulk CdO is only 2.3 eV, leading to relatively poor optical transparency in the short wavelength range, aliovalent metal doping offers the possibility of tuning the electronic structure and the optical band gap through a carrier density dependent Burstein-Moss shift. For all these reasons, CdO with simple cubic rock-salt crystal structure and small effective mass of conduction electron represents an ideal model material [2, 11].

In general, the electrical conductivity of TCOs can be enhanced either by increasing the carrier concentration or by improving the mobility of the carriers. Increasing carrier concentration can be achieved by heavy doping; however this will degrade the transparency due to increased free carrier absorption. Enhancing the mobility of charge carriers in TCOs will allow the conductivity to increase without compromising the transparency, thereby enhancing the overall performance of the TCO materials [11, 12]. Various dopants, including indium, tin, titanium, zinc, aluminum and fluorine, have been introduced into CdO to simultaneously increase the conductivity and widen the band gap due to alloying [13-15]. Yan et al. reported the epitaxial growth of tin doped CdO thin films on MgO by pulse laser deposition (PLD) with highest mobilities (600 cm$^2$/Vs) and with impressive electrical conductivity ($4.2 \times 10^3$ S/cm), rendering them the most conductive TCO thin films [16]. A variety of approaches for the preparation of undoped and doped CdO thin films have been employed via., physical and chemical deposition techniques, such as, electron beam evaporation [17], chemical spray pyrolysis [18], pulse laser deposition [19], successive ionic layer adsorption and reaction method (SILAR) [20], magnetron sputtering [21], metal organic chemical vapor deposition [22] etc.
In this chapter, we report the variation of structural and electrical properties of CdO thin films as a function of pH of spray solution by keeping other synthetic parameters such as substrate temperature, molarity of the spray solution and nozzle- to- substrate distance constant. A lot of work on the influence of deposition parameters such as substrate temperature, deposition time, molarity of precursor used etc. on the structural, optical and electrical properties has been reported by others [23-25]. To the best of our knowledge, no work on the influence of pH of spray solution on the opto-electrical properties of intrinsic CdO thin film is reported. Owing to the simplicity and inexpensiveness, spray pyrolysis technique has been employed to obtain high quality CdO thin films. Thus, highly conducting and transparent CdO thin films were obtained by spray pyrolysis simply by tuning the pH of the spray solution.

### 3.2. Preparation of CdO Thin Films

All the chemicals used were of analytical grade and were used without further purification. Cadmium acetate (Cd (CH$_3$COO)$_2$) of A.R grade was obtained from Himedia. Methanol, ammonia (24 %) and hydrochloric acid (HCl) were purchased from sd-fine, India.

Firstly, 0.04 M of cadmium acetate is dissolved in 30 ml methanol. CdO films are prepared by spraying the above solution on properly cleaned glass slides at temperature 375 °C in open conditions. The substrate temperature is optimized to 375 °C, since at higher temperature a significant decrease of the deposition rate was observed, which is attributed to a decrease of transport of mass towards the substrate due to rapid evaporation of the solvent. The deposition is done using our home built setup that is described elsewhere [26]. As the fine droplets of the spray solution reach the hot substrate, the pyrolytic decomposition of solution results in well adherent, uniform yellowish colored CdO films. To understand the effect of pH of spray
solution on the electrical properties of CdO thin films, spray solution with different concentration of ammonia and HCl, respectively, were prepared. The pH was measured and controlled by a pH-meter model DM-10 from Digimed. Sample S1, S2, S3 and S4 are prepared by dissolving 0.04 M cadmium acetate in methanol to which 400, 200, 80 and 40 µL HCl respectively is added and a total volume of 30 ml spray solution was used for deposition which yielded less conducting CdO films. Sample S5 was prepared by spraying 0.04 M cadmium acetate dissolved in 30 ml methanol at a substrate temperature of 375 °C in open conditions without any ammonia/HCl added to it, which is intrinsic one. Samples S6 and S7 respectively are prepared by dissolving 0.04 M cadmium acetate in the solvent mixture of volume ratio 1:5 and 5:1(ammonia: methanol) respectively to obtain highly conducting transparent films. Unlike ammonia, lower concentration of HCl is chosen, because more amount of HCl in the spray solution resulted in other amorphous complex phases such as chlorides and oxy-chlorides. The details of preparation conditions and their pH values are summarized in table 1. These films are then allowed to cool at room temperature and were further used for structural, optical and electrical characterizations.

3.3. Results and Discussion

3.3.1. X-Ray Diffraction Analysis and Surface Morphology

XRD spectra of CdO films are shown in figure 3.1. For clarity only XRD patterns of S1, S3, S5 and S7 are shown for comparison. The samples showed the characteristic peaks of (111), (200), (220) and (311) of cubic face centered phase of CdO (JCPDS card No. 05-0640 for CdO) and no secondary phases such as CdO₂ or Cd(OH)₂ were observed indicating it’s purity of single phase. The preferred orientation of CdO samples S1, S2, S3, S4 (prepared under the acidic conditions i.e. pH < 7) and S5 (prepared under neutral pH) respectively is along (111) direction, whereas for the
samples S6 and S7 (prepared for pH > 7) the preferred orientation is along (200) direction. It is important to mention that under pH < 7 the relative peak intensity

**Figure 3.1**: The X-ray diffraction pattern of CdO thin films prepared by varying the pH of the spray solution.
decreases even though the full width half maxima (FWHM) decreases resulting in larger grain size, whereas for pH > 7 the relative peak intensity increases considerably. With increase in ammonia concentration, the crystallinity of the films deteriorated, whereas for increase in HCl concentration, the crystallinity of the films enhanced considerably. The particle diameter $D$ is calculated using Scherrer formula, 

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

where $\lambda$ is X-ray wavelength, $\beta$ is full width half maxima and $\theta$ is the Bragg’s diffraction angle. Particle size for S6 and S7 are 25 and 22.8 nm respectively, whereas for S1, S2, S3, S4 and S5 the particle size ranges between 33–50 nm respectively. Similar results were also reported by other authors in case of pure CdO films where the preferential growth was observed along (111) direction [27, 28]. Maldonado et al. investigated the effect of pH (over a small range, at pH = 3.2 and 3.8) on the physical properties of In doped ZnO films by spray pyrolysis deposited over glass substrates at 500 $^\circ$C. Here, the electrical resistivity decreased with decrease in the pH while surface texturing increased with increase pH and the X-ray diffraction pattern showed (002) to be the preferential orientation for pH = 3.2, while it showed (002) and (101) to be the preferred orientation at pH = 3.8 [29].

Figure 3.2 depicts SEM micrographs of CdO films (S1, S3, S5 and S7). The SEM images showed that the surface morphology of the films depends on the pH of the spray solution. Films deposited at pH < 7 exhibited porous microstructures and spherical particles with some voids, whereas CdO films deposited at pH > 7 showed homogeneous and dense microstructures. Sivakumar et al. studied the influence of pH (over a wide range between 3 and 10) on ZnO nanocrystalline thin films prepared by sol-gel dip coating method. Here, the surface morphology improves with increase of pH values and the band gap energy decreased from 3.32 to 3.14 eV with increase in pH values [30]. In the present investigations, it is observed that the surface
Figure 3.2: Scanning electron micrographs of cadmium oxide thin films prepared by spray pyrolysis (a) S1, (b) S3, (c) S5 and (d) S7.

morphology and the grain size of the CdO films changed considerably as a function of pH of the spray solution.

3.3.2. Optical Absorption Measurements

The UV-vis absorption spectra of CdO thin films are recorded in the range 300-600 nm with glass as the reference; these are shown in figure 3.3. All the CdO films deposited as a function of pH of spray solution displayed the characteristic optical
band gap transition close to 475 nm corresponding to the band gap 2.62 eV. The edge associated with the longer wavelength shoulder corresponds to the fundamental absorption edge due to electron excitation from the valence band to conduction band.

Figure 3.3: UV-vis absorption spectra of cadmium oxide thin films deposited on glass substrate.
However, for the S1, that is prepared under more acidic condition, exhibits sluggish optical band gap absorption (in the range between 450 and 500 nm). In the expanded plot the absorption data of this sample shows the absorption edge related CdO. The optical band gap is estimated using the fundamental absorption. The absorption coefficient ($\alpha$) and the incident photon energy ($h\nu$) are related by the equation,

$$\alpha h\nu = A (h\nu - E_g)^n$$ \hspace{1cm} (3.1)

where, $A$ is a constant, $E_g$ is the band gap of the material and the exponent $n$ depends on the type $n = 1/2, 2, 3/2$ and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect respectively [21]. The present data fits well to $n= \frac{1}{2}$, indicating that CdO is a direct band gap semiconductor. The plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ was extrapolated to x-axis that gives the optical band gap of these films. The changes in the band gap for the films deposited at different pH are in the range 2.38 to 2.6 eV. The room temperature optical transmittance spectra in the wavelength range (300 – 1100 nm) of these films showed good transmittance (>70%) for the wavelength greater than 450 nm. The optical transmission of the samples increased with decrease in the pH of the spray solution.

3.3.3. Electrical Properties

Electrical conductivity measurements of CdO films deposited on glass were carried using the four probe technique. A home-built setup with soft electrical contacts (four probes) has been used. The variation in the physical properties such as resistivity, structure and morphology with respect to the pH of the spray solution could be associated to the chemical nature of the starting solutions. The various electrical parameters such as electrical resistivity ($\rho$), carrier density ($n$) and mobility ($\mu$) were determined using electrical conductivity and Hall effect measurements. The Hall measurements were carried out at room temperature under a magnetic field of 10 Kilo
Gauss and by passing a current of few milliamperes through the samples. Figure 3.4 shows semilogarithmic current-voltage curves for CdO films deposited by varying the pH of the spray solution and keeping all the deposition parameters constant. All the curves exhibit a linear relationship and hence are ohmic in the entire range of

Figure 3.4: Semi-logarithmic current-voltage curves of cadmium oxide thin films prepared by varying the pH of the spray solution.
measured voltage. For pure CdO (S5), the resistivity measured parameters constant. All the curves exhibit a linear relationship and hence are ohmic in the entire range of measured voltage. For pure CdO (S5), the resistivity measured x from $2.52 \times 10^{-3} \ \Omega \ cm$ (at pH 11.3) to $9.9 \times 10^{-4} \ \Omega \ cm$ (at pH 12.7). The low resistivity of the CdO thin films is associated with its native defects of oxygen vacancies and cadmium interstitials. The variation of resistivity as a function of pH of spray solution is shown in figure 3.5(a). It is clear that, initially there is a drastic decrease in resistivity with increase in pH (up to 6) and it becomes quite gradual from thereafter (till up to pH ~ 13). It is interesting to note that, there is a significant change in electrical resistivity as a function of pH value; in the present case it is almost by three orders of magnitude. 

Ravaro et al. studied the electrical properties of SnO$_2$ thin films obtained from colloidal suspension with distinct pH (at pH = 4, 5, 7, 9, 10 and 12). Here the decrease in pH leads to increasing electrical conductivity and larger crystallite size [31]. In the present work, the samples prepared under high pH values (i.e. pH = 11.3 and 12.7), showed good electrical conductivity with smooth surface texturing whereas films prepared under lower pH values showed poor electrical conductivity with poor homogeneity and non-uniform coating.

The general expression for electrical resistivity ($\rho$) is given by, $\rho = 1/ne\mu$, where the resistivity is inversely proportional to carrier concentration (n) as well as mobility ($\mu$). The subsequent increase of the resistivity at pH < 7 could be associated to the saturation in the mobility and small increase in the carrier concentration; this maybe due to large voids and poor bridging among CdO nanoparticles [32]. The variation of mobility and carrier concentration respectively as a function of pH of spray solution is shown in figure 3.5(b). Sample S5 exhibits a carrier concentration $7.6 \times 10^{19} / \text{cm}^3$ (at pH 7.4). This value increases with increase in pH at a maximum.
Figure 3.5: (a) A graph of resistivity of CdO films as a function of pH of spray solution. (b) Charge carrier concentration and mobility as a function of pH of spray solution. The solid lines that connect the data points are merely guide to eyes. These values are estimated using Hall effect and electrical conductivity measurements.
value of $5.1 \times 10^{20} / \text{cm}^3$ (at pH 12.7) followed by a decrease for lower pH values. Carrier mobility decreased gradually from 13.8 to 1.2 cm$^2$/Vs. The lower value of mobility is a consequence of rapid increase of carrier concentration, which lowers the mobility due to more charge carrier scattering.

Generally, undoped CdO samples show high n-type conductivity due to the presence of interstitials Cd atoms and oxygen vacancies which both act as donors. Murthy et al. studied the thickness dependent electrical properties of undoped CdO thin films prepared by spray pyrolysis method. The electrical properties of CdO films viz. resistivity, sheet resistance, carrier concentration and mobility were found to vary from $1.56 - 5.72 \times 10^{-3} \Omega \text{cm}$, 128 - 189 $\Omega$, $1.58 - 3.9 \times 10^{21} \text{cm}^3$ and $0.3 - 3 \text{cm}^2$/Vs for film thickness ranging from 200 – 600 nm [33]. Recently, Gokul et al. studied the effect of annealing on the physical properties of CdO thin films prepared by SILAR method. The carrier concentration, mobility and resistivity of about $1.26 \times 10^{22} \text{cm}^{-3}$, 0.05 cm$^2$/Vs and $8.7 \times 10^{-3} \Omega \text{cm}$ were achieved for the film annealed at 450 $^\circ$C [34]. In the present work, electrical resistivity $9.9 \times 10^{-4} \Omega \text{cm}$ ($n = 5.1 \times 10^{20} \text{cm}^{-3}$, $\mu = 12.4 \text{cm}^2$/Vs) with 70% transparency is obtained for CdO thin films deposited under alkaline conditions (pH ~ 12). Thus without extrinsic doping of CdO and due to its natural donor defects, which are most likely oxygen vacancies, CdO samples exhibited very good electrical conductivity. Hence a superior electrical conductivity (resistivity close to $9.9 \times 10^{-4} \Omega \text{cm}$) has been observed due to the better mobility of charge carriers. This could be due to enhancement in the grain size and reduction in grain boundary defects.

3.4. Conclusions

The CdO thin films with n-type conductivity have been prepared by chemical spray pyrolysis on glass substrate at 375 $^\circ$C. The pH of spray solution was found to have
strong influence on the surface morphology and electrical properties of spray pyrolysed CdO thin films and they are polycrystalline with cubic structure. For pure CdO and for samples with pH < 7 (acidic conditions) the preferred orientation is along (111) directions and that for samples (S6, S7) with pH >7(alkaline conditions) the preferred orientation was along (200) direction. A lowest resistivity of $9.9 \times 10^{-4}$ $\Omega$ cm ($n = 5.1 \times 10^{20}$ cm$^{-3}$, $\mu = 12.4$ cm$^2$/Vs) was obtained for CdO thin films deposited under alkaline conditions. The resistivity of CdO films increased by nearly two orders of magnitude for samples deposited for pH < 7 and it decreased by one order of magnitude for samples deposited for pH >7 and all the samples showed an optical transmittance in the range from 65% to 80 %. Thus, the electrical conductivity of CdO

Table 3.1: The details of preparation conditions for CdO films are given above. The glass substrate temperature was maintained at 375 °C for all the samples and the molarity of 0.04 M of cadmium acetate is chosen for the present work. The electrical parameters such as electrical resistivity, carrier concentration and mobility of CdO thin films are also mentioned below

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>pH of spray solution</th>
<th>Resistivity ($\Omega$ cm)</th>
<th>Carrier concentration ($\text{cm}^{-3}$)</th>
<th>Mobility ($\text{cm}^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>4.7</td>
<td>0.6435</td>
<td>$8 \times 10^{17}$</td>
<td>1.2</td>
</tr>
<tr>
<td>S2</td>
<td>5.9</td>
<td>0.199</td>
<td>$2.6 \times 10^{18}$</td>
<td>12.17</td>
</tr>
<tr>
<td>S3</td>
<td>6.5</td>
<td>$1.3 \times 10^{-2}$</td>
<td>$3.8 \times 10^{19}$</td>
<td>12.36</td>
</tr>
<tr>
<td>S4</td>
<td>6.8</td>
<td>$1.1 \times 10^{-2}$</td>
<td>$4.6 \times 10^{19}$</td>
<td>12.3</td>
</tr>
<tr>
<td>S5</td>
<td>7.4</td>
<td>$6.7 \times 10^{-3}$</td>
<td>$7.6 \times 10^{19}$</td>
<td>12.2</td>
</tr>
<tr>
<td>S6</td>
<td>11.3</td>
<td>$2.52 \times 10^{-3}$</td>
<td>$1.79 \times 10^{20}$</td>
<td>13.8</td>
</tr>
<tr>
<td>S7</td>
<td>12.7</td>
<td>$9.9 \times 10^{-4}$</td>
<td>$5.1 \times 10^{20}$</td>
<td>12.4</td>
</tr>
</tbody>
</table>
films could be easily tuned by simply varying the pH of spray solution without compromising the transparency and keeping the other deposition parameters fixed.
References


