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Original Article

Structural and Optical Characterization of Nanostructured CdO:Sn Thin films prepared by Chemical Spray Pyrolysis Technique

K. Kesavan, V. Manivannan, S. Krishnaraj, R. Ashok Kumar

Periyar Maniammai University, Thanjavur, Tamil Nadu, India-613 403

PRIST University, Thanjavur, Tamil Nadu, India-613 403,

Mannai Rajagopalam Govt. Arts College, Mannargudi, Tamil Nadu, India.

Corresponding Author:

Email id.: kk7blr@gmail.com

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Abstract

A great deal of research efforts was directed towards investigation of the physical properties of thin film to improve the quality and performance of the device and for finding new applications. In this study, undoped cadmium oxide (CdO) and tin doped cadmium oxide (CdO:Sn) films were deposited onto glass substrates by home built spray pyrolysis technique at 250ºC temperature. The structure of the undoped and tin doped films were studied by X-ray diffraction have polycrystalline structure with (111) and (200) preferential orientations. X-ray peak line was studied to estimate grain size, strain and other orientations. The transmittance in visible and NIR region with direct optical band gap was estimated for undoped CdO and Tin doped CdO. The results are analyzed for three different volume of precursor solution and three different concentrations of Tin doped CdO films and are reported.

Keywords: Thin films, Spray pyrolysis, cadmium Oxide, Diffraction and optical studies.

1.1 Introduction

The transparent conducting oxide thin films such as zinc Oxide (ZnO), Indium tin oxide (ITO), tin oxide (SnO2) and cadmium oxide (CdO) etc., are attracted researchers due to their high quality of optical and electrical properties and extensively used in semiconductor optoelectronic applications [1-3]. CdO is an n-type semiconductor with a rock-salt crystal structure (FCC) and posses direct band gap between (2.3eV and 2.5eV)[4]. Its high electrical conductivity (even without doping) and high optical transmittance in the visible region of solar spectrum[5] which has found extensive applications in solar cells[6], low emissive window optical communications, flat panel display, photo transisitors[12,15], photo diodes[12,15], liquid crystal display [12,14], photovoltaic cell [12,14], optical heaters [16], IR detectors [12,13], transparent electrodes and gas sensors [7-11].

There are variety of deposition techniques reported in the literature to obtain CdO samples, such as sol-gel technique [19], solution growth [18], pulsed laser deposition [20], MOCVD [21], chemical bath deposition [17], and spray pyrolysis [16]. Amongst all the above deposition techniques, chemical spray pyrolysis techniques is a simple, cost effective, and suitable technique for good thickness uniformity over a large area deposition of many binary, ternary and quaternary semiconducting thin films with various concentrations. It is an effective production technique to lead to short production time, homogeneous particle composition with controlled particle size [23] and one step production method [22]. In an ideal condition, due to optimum temperature the spray pyrolysis deposition films are obtained when the droplet approaches the substrate just as the solvent is completely vaporized. It is also a versatile method for producing a wide range of composition of various materials.

The present work deals the structural and optical studies of undoped and tin doped cadmium oxide thin films deposited by chemical spray deposition technique.

1.2 Materials and Methods

Cadmium oxide thin films were deposited on the glass substrate from aqueous solution of cadmium acetate with a concentration of 0.05M dissolved in 50ml of double distilled water. For tin doping, different concentration 0.1x10^{-3}M, 0.2x10^{-3}M and 0.3x10^{-3}M of stannic chloride was dissolved in distilled water of 25ml and both are mixed.
and stirred for 20 minutes at room temperature to form a 50ml precursor solution. Prior to spraying the precursor solution, the glass substrates were cleaned by soap solution and acetone, and dried. The precursor solution is deposited by chemical spray pyrolysis method onto the preheated glass substrates kept at the temperature of 250°C. In order to maintain the constant temperature of 250°C, the temperature of hot plate of electric furnace kept in the tightly closed room is controlled by thermo-controller. The double wall glass nozzle designed was placed at a distance 30cm from the substrate. The solution was sprayed by nozzle tip which was kept at an angle of 45° with respect to substrate. The successive spray time was 5 seconds for spraying and 15 seconds left for avoiding excessive cooling of substrate and to maintain constant temperature on surface of the substrate. The films were prepared with 50ml of solution which was sprayed by successive spray method for 30-35 minutes at constant flow rate 3ml/min via compressed carrier gas. Compressed carrier gas released from air compressor which is kept at a pressure of 2 Kgcms⁻² flows through the air filter and regulator to get a fine mist of spray. The Sn doped CdO thin films were prepared with different concentration with various volume of the precursor solution which is shown in table 1.

The structural, optical, and morphological studies were investigated using X-ray diffractometer, optical spectrometer, and scanning electron microscope (SEM), and reported.

1.3 Results and discussion

The structural analysis was carried out by recording X-ray diffraction (XRD) spectrum using X-ray diffractometer (PANalytical X’Pert) recorded in the 2θ range from 10º to 90º with step size of 0.02º using cu-Kα radiation (λ=1.54056Å ). The X-ray diffraction patterns of undoped and Sn doped thin films for different volumes (10, 30 and 50ml) of precursor solution are shown in figure 1 (a, b & c). The obtained X-ray diffraction spectra are compared with JCPDS card [005-0640] indicating polycrystalline nature with face centered cubic crystal structure. The planes are indexed as (111), (200), (220), (311) and (222) with respect to standard card, and X-ray diffraction lines shows broadened in their shape. When the volume of precursor solution increased for the deposition,

![Figure 1. XRD pattern of various concentration of Sn doped CdO thin films with different volumes (a) 10 ml, (b) 30ml and (c) 50ml](image)

the intensity of all the peaks are increased and the preferential growth along (111) and (200) planes are observed for undoped CdO films and Tin doped CdO films. The preferential orientation is changed from (111) plane to (200) plane, for the changing concentration of tin at the same deposition temperature of the films. The intensity of preferential peak of plane (111) shifted slightly towards the (200) plane when Sn doping concentration increases, which implies that doping Sn²⁺ substituting Cd²⁺ position in CdO crystal induced the lattice shrinkage, since the covalent radius of Sn (1.41Å) is slightly smaller than that of Cd (1.48Å).

1.3.1 Grain size and Strain analysis

Figure 2(a & b) shows that the grain size is lesser and higher strain for the film deposited at lower concentration. X-ray line broadening technique is also adopted to determine small crystallite (grain) size of the film by utilizing Scherrer formula [12] for preferential plane (111).

\[
D = \frac{K\lambda}{\beta\cos\theta}
\]

Where ‘β’ is the breadth of the diffraction line at its full width half maximum intensity (FWHM) in radians, ‘λ’ is...

Figure 2: Variation of (a) grain size (b) strain for the preferential peak (111) of different Sn concentration and volume of precursor solution.

Figure 3: SEM images of CdO:Sn thin films deposited with different volume of precursor (a) 10ml, 0.1×10^{-3}M, (a) 50ml, 0.1×10^{-3}M, (b) 10ml, 0.2×10^{-3}M, (b) 50ml, 0.2×10^{-3}M, (c) 10ml 0.3×10^{-3}M and (c) 50ml, 0.3×10^{-3}M
the wavelength of the incident X-ray (1.541 Å), $\theta$ is the angle at which the maximum peak occurs and 'K' is the shape factor which usually takes a value of about 0.89. The grain size increased rapidly upon increasing the Sn concentration as well as volume of precursor solution. The grain size of the undoped film was found to be 43nm-51nm for 10-50ml precursor solution and the doped thin film changed in the range of 38nm-54nm for the different concentrations of Sn.

It is observed from figure 2(a) the grain size is increased as precursor solution concentration increased until 0.2x10^{-3}M further increasing the concentration the grain size would be decreased. The uniform compressive or tensile strain (macrostrain) results in peak shift [13] of X-ray diffraction lines. A non-uniform of both tensile and compressive strain results in broadening of diffraction lines (microstrain).

Increase in grain size decreases the microstrain which indicates peak movement without changing the shape of the peak. For the minimum volume of the precursor solution (10ml) when the doping concentration increases the grain size will also be slightly increased. From the figure 2(a & b), we can conclude that the maximum grain size and minimum strain have to be attained at higher volume of 0.2x10^{-3}M concentration.

1.3.2 Morphological Studies

The morphological microstructure of Tin doped CdO films were investigated by using TESCAN Vega scanning electron microscope with an accelerating potential of 15 kv as shown in figure 3. The film has porous nature with grains like morphology. It represents that CdO:Sn particles deposited on the surface of the glass substrate and forms as spherical shape grains like morphology. Each grain can be indexed to have cubic crystalline. It consists of tightly packed uniform spherical shape grains without crack. This indicates the film is well adherent with substrate. The micrographs, a, b and c in figure 3 represents 10 ml volume of precursor solution deposited at constant temperature 250°C±5°C. It can be observed some places are highly porous due to the presence of the holes at the surface also makes the surface rough. However, when the volume of precursor solution increased to 50ml, the porous structure becomes dense and a relatively flat surface with a cluster of particles can be seen for the micrographs as shown in Figure 3(a1, b1 & c1). X-ray diffraction pattern also confirm enhancement of the crystal quality with increasing volume of the precursor solution. These are found to be high quality, good uniformity, high transmittance and good crystallinity. It is evident from these microphotographs that the surface roughness of the film decreases with increasing Sn doping level. Thus the surface roughness of CdO films could be controlled by Sn doping.

Figure 3 indicates surface morphologies of Sn doped CdO thin films with different volumes (10, 50ml) and concentrations (0.1x10^{-3}M, 0.2x10^{-3}M and 0.3x10^{-3}M). It can be seen that the grain size of pure CdO film is about ~43nm. The grain sizes of thin films are about ~38nm, ~39nm, ~34nm, ~44 nm and ~51nm for the volume – concentration combinations {10ml, 0.1x10^{-3}M}, {50ml, 0.2x10^{-3}M}, {10ml 0.3x10^{-3}M} and {50ml, 0.3x10^{-3}M} respectively.

The increase of grain size means improved crystallinity and the decrease of total grain boundary fraction in the thin films, which can be reduced grain boundary scattering and also decreased of electrical resistivity [15]. The grain size as seen from the image is comparable with the X-ray diffraction studies.

1.3.4 Optical characterization

In order to analyze optical properties of deposited films, it has to be determined the absorbance, transmittance, refractive index and band gap. Optical transmission and absorption spectra were recorded in the wavelength region 200nm-1200nm. The Sn doped CdO
thin films are light-yellow but highly transparent. The color of the film becomes dark with increase of volume of precursor solution and lighter with the increase of Sn concentration. Figure 4 shows smooth increase in transmission from 550nm to 900nm, which reveals high transparency in visible and NIR regions and it is in good agreement with the reported results from literature [14]. This smooth increase is due to crystalline nature of prepared films. The maximum transmission is found to be 88% at 900nm. The optical transmittance and absorption edge of the spectra for the CdO:Sn thin films are varied with different volume of spray solution and Sn concentration. Optical absorption loss increases and transmittance decreases in the visible region with increasing Tin content in CdO films. The absorption coefficient $\alpha$ is calculated from Lamberts law

$$\alpha = 2.303 \frac{A}{t}$$

Where A is optical absorbance and $t$ is the thickness of the film obtained by Mitutoyo profilometer.

The transmittance curve recognizes the smooth increase of transmission in the visible region and attained maximum transparency (< 85%) in the NIR region which reflects nature of the film. Transmittance of the film decreases with increasing the volume of spray solution from 10ml to 50ml and increasing Sn doping concentration (0.1x10^-3 - 0.3x10^-3 M). Transmittance decreases at higher
doping level and this may be due to the scattering of photons by crystal defects or probably due to the increase in the metal to oxygen ratio [16]. In fact the ‘metal to oxygen ratio’ determines the transmittance [17, 18] and if the sample is metal rich, it will have low transmittance. Therefore the film acts as a ‘metal like’ mirror in NIR region. It is interesting that with an increase of Sn doping concentration, the absorption edge of CdO:Sn thin films are blue-shifted in the range of 300-500nm. It is quite clear that as doping concentration increased the (Cd+Sn)/O ratio is also increased, grain size and surface roughness increases, which leads to the reduction in optical transmission. Figure 4(a-c) shows that all the films have transmission above 75% in the visible and NIR region. From the table 2, it can be concluded that the transmission enhances in the visible region at the Sn concentration level (0.2×10⁻³M) in CdO. In the case of a transparent conducting oxide film, optical transmission has to be as large as possible for the application in the optoelectronic devices.

From the plot between (αhv)² and hv, it is linear over a wide range of photon energies, indicating direct band to band transition as shown in figure 5(a-c). Small variation of band gap was observed for increasing Sn doping and no variation of band gap for the change of volume of solution. Where hv is photon energy and ‘α’ is the absorption coefficient expressed as

\[ \alpha = \frac{\ln \left( \frac{1}{T} \right)}{d} \]

Where ‘T’ is transmittance and ‘d’ is film thickness. The obtained band gap value (2.5eV) for CdO film is in agreement with the literature value [19]. The blue shift of the absorption edge of CdO:Sn thin films can be obtained by increase in Sn concentration which is known as the Bursteine Moss (BM) effect [20,21]. When the doping concentration increased, it can block the lowest state in the conduction band, which may lift the Fermi level up to the conduction band of the semiconductor which leads to energy band broadening. Thus, widen bandgap has remarkable practical significance. Such as TCO films used in solar cell applications that are always required higher bandgap. In the present study, bandgap can be obviously increased from 2.5eV for CdO film to the higher level 2.65eV significantly for CdO:Sn thin films.

The refractive index is one of the important parameter for optical materials and its applications. The reflection and absorption effects due to the substrate were removed from the measured data. The refractive index of the films was determined with reflection (R) from the following relation [22]

\[ n = \frac{1 + R}{1 - R} + \frac{4R}{(1 - R)^2 - k^2} \]

Where \( k = \alpha \lambda / 4 \pi \) is the extinction coefficient. Figure 6 presents variation of ‘n’ and ‘k’ values with wavelength, which indicates the refractive index values linearly varying from 500nm- 900nm and are reported in the table 3. In the wavelength range 800nm - 900nm, 80 to 85% of the light was transmitted, which is commonly used for optical fiber communication. It can be concluded that the refractive index of undoped CdO is1.2509 and increased significantly for higher concentration of Sn-CdO thin films.

**CONCLUSIONS**

X-ray diffraction, SEM and optical properties were investigated for Undoped and Sn doped CdO films. X-ray diffraction pattern confirms CdO phase with preferential orientation along (111) and slightly shifted to (200) for higher concentration of Sn. The grain size increases for increasing the Sn concentration. The grain size of the doped film was increased and attained maximum size 54nm at 0.2×10⁻³M concentration of Sn. Surface morphology studies shows that the CdO:Sn was grown as

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**Table 1.** Three different Concentrations and three different volumes of CdO:Sn thin films.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cadmium acetate in ml</th>
<th>Stannic chloride in ml</th>
<th>Volume of solution in ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdO : Sn 25 (0.05M)</td>
<td>25 (0.1x10⁻³M)</td>
<td>10,30,50</td>
<td></td>
</tr>
<tr>
<td>CdO : Sn 25 (0.05M)</td>
<td>25 (0.2x10⁻³M)</td>
<td>10,30,50</td>
<td></td>
</tr>
<tr>
<td>CdO : Sn 25 (0.05M)</td>
<td>25 (0.3x10⁻³M)</td>
<td>10,30,50</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2: Comparison of optical transmittance of CdO and CdO:Sn thin films**

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>CdO 0.05M</th>
<th>CdO:Sn 0.050:1x10⁻³M</th>
<th>CdO:Sn 0.050:2x10⁻³M</th>
<th>CdO:Sn 0.050:3x10⁻³M</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ml</td>
<td>28.92</td>
<td>5.52</td>
<td>3.67</td>
<td>2.58</td>
</tr>
<tr>
<td>30 ml</td>
<td>50 ml</td>
<td>62.65</td>
<td>45.09</td>
<td>37.10</td>
</tr>
<tr>
<td>900</td>
<td>90.50</td>
<td>88.78</td>
<td>87.95</td>
<td>86.35</td>
</tr>
</tbody>
</table>

**Table 3: Refractive Index of Undoped and Sn doped CdO**

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>Undoped</th>
<th>0.1x10⁻³M</th>
<th>0.2x10⁻³M</th>
<th>0.3x10⁻³M</th>
</tr>
</thead>
<tbody>
<tr>
<td>918</td>
<td>1.2509</td>
<td>1.2598</td>
<td>1.3547</td>
<td>1.4547</td>
</tr>
<tr>
<td>550</td>
<td>2.3260</td>
<td>2.1306</td>
<td>2.3044</td>
<td>3.5232</td>
</tr>
<tr>
<td>300</td>
<td>41.9909</td>
<td>21.3066</td>
<td>15.5506</td>
<td>51.6772</td>
</tr>
</tbody>
</table>
spherical shape grains and have good adherent. Films have good transmission in upper visible region and NIR region. The transmission of the film was more than 78% and the presence of Sn increases the refractive index of the film. The graph was extrapolated to give band gap (Eg) value was found to be 2.5eV – 2.65eV. Finally, it has been concluded that Sn doped CdO films have enhanced properties and a good candidate for photovoltaic applications.

References


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