ABSTRACT

Cadmium oxide (CdO) thin films have been deposited by a locally developed spray pyrolysis method onto glass substrate at 473K. The optical and electrical properties of the as-deposited and annealed films are studied in details. The surface morphology of the samples was studied by scanning electron microscopy (SEM). The SEM micrograph of as-deposited film shows uniform deposition over the substrate well. The optical absorption coefficient ($\alpha$) of the CdO films was determined from transmittance spectra in the range of wavelength 450 – 650nm. For different thicknesses (130nm ~ 380nm) of as-deposited films, the direct band gap is found in the range of 2.40 ~ 2.51 eV and indirect band gap in the range of 1.97 ~ 2.20 eV. Resistivity ($\rho$) of CdO thin film was measured in the temperature range of 303 to 553K. The resistivity of the films of different thickness initially increases with increase in temperature and reaches a maximum at 430K and then decreases with further increase of temperature. The resistivity of the film exhibits metallic behaviour up to 430 K and above that the film behaves like a semiconductor. Activation energy ($\Delta E$) in the semiconductor region is found in the range from 0.049 to 0.075 eV for films of thickness ranging from 160 - 285 nm.

Keywords: Spray pyrolysis, CdO, Resistivity, Optical band gap, Activation energy

INTRODUCTION

The study of transparent conducting oxide film such as cadmium oxide (CdO) has been given much effort because of its wide range of technical and industrial applications, especially in the field of optoelectronic devices such as solar cells\cite{1,2}, photo transistors\cite{3} and diodes\cite{4}, transparent electrodes\cite{5}, gas sensors\cite{6}, etc. CdO thin films exhibit high transmission in the visible and UV regions, as well as a high ohmic conductivity. Bulk CdO shows n-type conductivity mainly due to oxygen vacancies. In the last decade, various techniques such as thermal evaporation\cite{7}, sputtering\cite{8}, solution growth\cite{9}, pulsed laser sputtering\cite{10}, activated reactive evaporation\cite{11} and spray pyrolysis deposition (SPD)\cite{12} were employed to prepare thin films of CdO.

CdO thin films were deposited by thermal evaporation\cite{7} under vacuum onto glass substrates kept at 300 and 473K. The optical energy band gap was found 2.4 eV\cite{13}. Thin films of CdO were deposited onto amorphous and fluorine-doped tin oxide (FTO) glass substrate using SPD technique\cite{14}. In this study, direct band gap energy was found 2.26 eV. The electrical resistivity ($\rho$) is of the order of $10^3$ Ohm-cm and it decreases with
increase in temperature indicating semiconducting nature. Uplane et al.\textsuperscript{(12)} reported the preparation of CdO thin films on glass substrate at 400°C by spray pyrolysis. Varkey and Fort \textsuperscript{(9)} prepared transparent CdO thin films on glass substrate using aqueous solution of soluble cadmium amine complexes as a precursor of CdO. It was experimentally established that the electrical and optical properties are very sensitive to film structure. The best performances depend on the surface and interface properties of the deposited films. The excellent features, good controllability, high repeatability and fast response depend on the various deposition parameters like spray rates, molar concentrations, substrate temperatures, and deposition time etc.

In recent years, researchers are trying to modify the synthesis procedure with an aim to improve the chemical and physical properties of CdO films. In this paper, we have deposited CdO thin films onto glass substrate by a locally developed SPD technique because it is more attractive and advantageous for its simplicity, cheapness, low cost of starting material and capability of large area deposition. Detailed optical and electrical properties of CdO thin films have been investigated for various film thicknesses. The influence of annealing temperature on the film characteristics has been investigated. We have compared the results of our as-deposited CdO thin films with the characteristics reported by other researchers \textsuperscript{(13-14)}.

**EXPERIMENTAL**

The spray pyrolysis deposition of CdO thin films was carried out in a locally made reaction chamber. The deposition set up consists of four sections, which include (a) the precursor solution and carrier gas (air) assembly connected to the spray nozzle, (b) the reaction chamber in which the substrate is heated, (c) the pumping and exhausting gas scrubbing systems, and (d) temperature controller with a Copper-Constantine thermocouple to control the substrate temperature.

In the present work, precursor solution of 0.1M of Cadmium acetate was used as raw material to deposit CdO thin films. The solution was sprayed onto pre-cleaned glass substrate. The substrate temperature was maintained constant at 573K. The normalized distance between the spray nozzle and the substrate was fixed at 29 cm. The pressure of the carrier gas (air) was kept constant at 1 bar. The solution flow rate was maintained 0.5 ml min\textsuperscript{-1} throughout the experiment. Films of various thicknesses were prepared through different deposition times.

The possible chemical reaction that takes place on the heated substrate to produce CdO may be as follows:

\[
\text{Cd(OCOCH}_3\text{)}_22\text{H}_2\text{O} \xrightarrow{300^\circ \text{C (deposited)}} \text{CdO} + \text{CO}_2 + \text{CH}_4 + \text{steam}
\]

Thickness of the films was measured employing interference Newton’s ring method. The surface structural properties of the films were examined by Scanning Electron
Microscopy (SEM). The optical transmission spectra for as-deposited and annealed CdO thin films of different thicknesses were obtained in the visible region (400-1100 nm) using UV-VIS spectrophotometer (Model: pc1601, Shimazdu). The experimental accuracy of the transmittance is (± 0.005%) and of the wavelength is (± 0.005%). The observed transmittance data were corrected relative to optically identical uncoated glass substrate. D.C Electrical resistivity measurements were made in air for freshly deposited films from room temperature, 300 to 553 K by Van der Pauw method\(^{(15)}\) and measurements were performed by increasing the temperature slowly of the film. The films were annealed up to a maximum temperature of 553 K for one hour. Resistivity measurements were then reversed by decreasing the temperature slowly to room temperature. Samples were again heated slowly and resistivity was again measured.

RESULTS AND DISCUSSION

Surface morphology

Fig.1 shows the SEM micrographs of as-deposited and annealed CdO thin films. The films deposited by SPD method is generally polycrystalline or amorphous in structure. Fig 1(a) shows uniform deposition of CdO thin film and covers the substrate well. Figures 1(b) and (c) show micrographs of annealed samples at different temperatures. Annealing at higher temperature increases the grain size because of an increase in surface mobility. Under heat treatment the materials pass through some breaking of weakly attached bonds. Bond breaking products are evaporated in the gaseous form as CO\(_2\) and others. After removal of gaseous products some voids are found on the sample surface. After annealing the surface roughness is found to increase.

Hence the sprayed particles (atoms) are adsorbed onto the surface to form clusters as the primary stage of nucleation having higher energy than the individual atoms. Therefore at higher annealing temperature, growing nuclei come into contact to form island pattern and appears as spheroid shape.

Optical Properties

The transmission spectra for as-deposited and annealed CdO thin films in the wavelength range (400-1100nm) are shown in Fig.2. The as-deposited film onto heated substrate shows high transmittance and the annealed film results in a small decrease of transmittance due to Cd precipitation in the transition from amorphous into polycrystalline structure.

At higher temperatures, the film surface became powdery because of homogeneous nucleation and reaction. Variation of optical absorption coefficient with photon energy for various film thicknesses is shown in Fig.3. The absorption coefficient (\(\alpha\)) is calculated from the transmittance spectrum using the relation

\[
\alpha = \frac{\ln(\frac{1}{T})}{t}
\]
where $T$ is the transmittance and $t$ is the thickness of the film. It shows that the absorption co-efficient increases slowly at the higher wavelength region and then increases sharply near the absorption edge. The absorption co-efficient increases with the thickness of the film strongly demonstrating that the film property is thickness dependent.

Fig 1. SEM micrograph of CdO film (0.1M) (a) as-deposited at 573K for 10min, (b) annealed at 623K for 60 min (c) annealed at 673K for 60min.
A plot drawn between $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 4. The direct band gap energy of CdO has been obtained from the intercept of the straight line drawn from $(\alpha h\nu)^2$ versus $h\nu$ curve on the energy axis. Fig. 5 shows $(\alpha h\nu)^{1/2}$ versus $h\nu$. The indirect band gap has been determined by the similar way. The values of optical band gap obtained for direct and indirect transitions are shown in Table 1, which indicates that both direct and indirect band gap decreases with increase of film thickness (Fig. 6). Since CdO is an n-type semiconductor, the band gap decrease with the increase of film thickness, it could be due to the increase of density of localized state in the conduction band.

### Table 1

<table>
<thead>
<tr>
<th>Film thickness $t$ in nm</th>
<th>Direct band gap energy $E_g$ in eV</th>
<th>Indirect band gap energy $E_{ig}$ in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>2.51</td>
<td>2.20</td>
</tr>
<tr>
<td>150</td>
<td>2.49</td>
<td>2.13</td>
</tr>
<tr>
<td>230</td>
<td>2.47</td>
<td>2.10</td>
</tr>
<tr>
<td>350</td>
<td>2.44</td>
<td>2.05</td>
</tr>
</tbody>
</table>
Electrical Properties

Variation of resistivity with temperature during heating, cooling and reheating is shown in Fig. 7. Resistivity shows a non-reversibility behavior in the first heating and cooling cycle. However, resistivity shows reversibility on repeated cycle of heating and cooling and eventually retraces the similar path, indicating a stable state of the sample. The stability of the film seems to be due to the removal of metastable phases, in homogeneity, residual stress and defects that might be present in the prepared samples. From Fig. 7, it is clear that the resistivity of stable CdO is lower than the resistivity of the as-deposited films. This reduction in resistivity could arise due to the removal of defects after annealing. It is also observed that resistivity initially increases slowly with the increase of temperature, reaches to a maximum value at about 430 K and then decreases with further increase in temperature. Therefore it is assumed that in CdO, a phase change occurs at some critical temperature. Below that critical temperature, CdO film shows metallic behavior and above it, the film behaves as a semiconductor. A similar change in resistivity behavior with temperature above 430K is reported on CdO thin films(11). Fig 8. shows temperature dependent resistivity for a number of films of different thickness. All films show similar temperature dependence of resistivity, i.e., a phase change occurs for all films. It can be seen that the position of the maximum resistivity i.e., phase change temperature (T_P) shifts gradually towards higher temperature with increase in thickness of the films.
Fig. 7 Variation of resistivity with temperature

Conductivity of the CdO materials was calculated from the resistivity measurements. The conductivity initially decreases with increase in temperature. The value goes through a minimum and then increases with further increase of temperature. The minimum conductivity is observed near 470 K and the position of minimum conductivity shifts slowly towards the higher temperature with increase in thickness of the films. The overall conductivity increases with increase of film thickness. The increase in conductivity due to increasing thickness may be attributed to the increasing number of oxygen vacancies present in the sample. In both the temperature regions, the d.c. electrical conductivity for the thin films can be expressed by the usual relation

$$\sigma_f = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right)$$

where $\Delta E$ is the activation energy, $k$ is the Boltzmann constant and $\sigma_0$ is the pre-exponential factor. Following this relation, the activation energy ($\Delta E$) of the carriers for high temperature region was calculated from the slope of the plots. The values obtained are given in Table 2. The nature of the variation of conductivity with temperature suggests that more than one type of conduction is involved in CdO. In the low temperature region it shows metallic behavior and the conductivity decreases with the increasing temperature. This reduction in conductivity is due to the various types of scattering of carriers. In the high temperature region a phase change seems to occur and CdO shows semiconducting property. The activation energies are quite low. These low activation energies may be associated with hoping of carriers between the localized levels.

<table>
<thead>
<tr>
<th>Film thickness in nm</th>
<th>Activation energy $\Delta E$ in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>0.075</td>
</tr>
<tr>
<td>200</td>
<td>0.054</td>
</tr>
<tr>
<td>240</td>
<td>0.052</td>
</tr>
<tr>
<td>285</td>
<td>0.049</td>
</tr>
</tbody>
</table>

CONCLUSIONS

CdO thin films were prepared onto glass substrate keeping the substrate temperature 573K by spray pyrolysis method. Different physical properties such as optical and
electrical properties as well as surface morphology have been studied. The SEM micrographs of as-deposited film show uniform deposition over the substrate. After annealing the surface roughness increased due to absorption of sprayed particles (atoms) into the substrate to form clusters as the primary stage of nucleation. The absorption coefficient is obtained to be $10^4 \text{m}^{-1}$ at the higher energy region and the rate of absorption is maximum near the absorption edge at around 500 nm. The electrical measurements were made on the as-deposited films from the room temperature to 553K. The resistivity is found $10^4 \text{Ohm-cm}$ at room temperature. Conductivity shows two types of activation process within the measured temperature range. In the low temperature region CdO shows metallic nature. In the high temperature region activation energy varies from 0.049 eV to 0.075 eV depending on thickness and the conduction is mainly due to hoping of electrons. In this study, the results obtained from optical and electrical as well as surface micrographs are found to be in good agreement with the reported results (12-13). Although the spray pyrolysis method is an old technique but still it is useful for synthesis of quality thin films at low cost for both academic and scientific interest.

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