Temperature Dependent Structural and Optical Properties of Nanostructured Cr Doped CdO Thin Films Prepared by DC Reactive Magnetron Sputtering

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Abstract

Nanostructured Cr doped CdO thin films were deposited by DC reactive magnetron sputtering technique on glass substrates at different substrate temperatures. The structural, electrical and optical properties of Cr doped CdO films were investigated. From XRD data, all the films are highly oriented in the (2 0 0) direction. Surface morphology of the samples has been studied using FESEM and the elemental composition of the films is determined from EDS spectra. The minimum resistivity of \(1.92 \times 10^{-4} \Omega \cdot \text{cm}\) is obtained for the thin film deposited at substrate temperature of 350 \(^\circ\)C. The optical transmittance of Cr doped CdO thin films increases with the increase of substrate temperature from room temperature to 350 \(^\circ\)C. The optical absorption edge of the films is shifted towards lower wavelengths with increase in the substrate temperature. The optical direct band gap values of Cr doped CdO films increased with the increase of substrate temperature. The increase in optical band gap may be due to improvement in crystallinity of the films and Burstein-Moss shift.

Keywords: Sputtering; Thin films; X-ray diffraction; Electrical properties; Optical properties

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1. Introduction

Transparent conducting oxide (TCO) films have high technological potentials in the field of optoelectronic and other solid state devices. TCOs are essential part of technologies that require both large area electrical contact and optical access in the visible portion of the light spectrum. The various TCOs include the oxides of Sn, In, Zn, Cd and their alloys. Cadmium oxide is an n-type semiconducting material with higher mobility. Cadmium oxide in the form of transparent conducting film has been used in various applications such as photodiodes, phototransistors, photovoltaic cells, LCD (Liquid Crystal Display), gas sensor, thin film resistors etc., (Zhao et al. (2002), Mane et al. (2006), Lewis and Paine (2000)). Chromium doping of CdO is efficient in construction electronic transport ways for obtaining high mobility in comparison with other dopants and could be successfully used for technical applications based on its IR-TCO characteristics (Mishra et al. (2009) and Hames et al (2004)). It was observed that dopant ions of slightly smaller size than that of Cd$^{2+}$ could improve the electronic conductivity and mobility. The Shannon ionic radius (Shannon (1976)) of Cd$^{2+}$ is 0.095 nm for coordination number CN = 6 of the CdO structure while it is 0.0615 nm for Cr$^{3+}$ ions for the same coordination number, CN = 6. Thus, the ionic-radius difference is 35%. In the present study for the first time we have reported Cr doped CdO thin films deposited on glass substrates by DC reactive magnetron sputtering method at different substrate temperatures. The aim of the present work is to study the structural, electrical and optical properties of Cr doped CdO films.

2. Experimental details

Cr doped CdO thin films were prepared by DC reactive magnetron sputtering technique at different substrate temperatures. High purity of Cadmium (99.99%) and Chromium (99.99%) targets with 2 inch diameter and 4 mm thickness are used for deposition on glass substrates. The base pressure in chamber was 3 x 10$^{-6}$ Torr and the distance between target and substrate were set at 60 mm. The glass substrates were ultrasonically cleaned in acetone and ethanol, rinsed in an ultrasonic bath in deionized water for 15 min, with subsequent drying in an oven before deposition. High purity (99.99%) Ar and O$_2$ gas was introduced into the chamber and was metered by mass flow controllers for a flow rate fixed at 30 sccm for Ar and 2 sccm for O$_2$. Deposition was carried out at a working pressure of 3 mTorr after pre-sputtering with argon for 10 min. The DC sputtering power maintained at the time of deposition for Cd target is 85 W and 40 W for Cr target. Film thickness was measured by Talysurf thickness profilometer. The resulting thicknesses of the films are found to be ~350 nm. X-ray diffraction (XRD) patterns of the films were recorded with the help of Philips (PW 1830) X-ray diffractometer using CuK$\alpha$ radiation. The tube was operated at 30 KV, 20 mA with the scanning speed of 0.03(2$\theta$)/sec. Surface morphology of the samples has been studied using HITACHI S-3400 Field Emission Scanning Electron Microscope (FESEM) with Energy Dispersive Spectrum (EDS). EDS is carried out for the elemental analysis of prepared thin film samples. The electrical resistivities of the films ($\rho$) were measured using the four-point probe method. Optical transmittance of the films was recorded as a function of wavelength in the range of 300 – 2500 nm using JASCO Model V-670 UV-Vis-NIR spectrophotometer (Japan).

3. Results and discussion

The XRD patterns of Cr doped CdO thin films deposited on glass substrates as function of substrate temperatures are shown in Fig. 1. All the films are highly oriented in the (2 0 0) direction. The intensity of the (2 0 0) peak increases with the increase of substrate temperature, indicating that the films at higher temperature have a higher crystalline quality. Some other peak corresponding to (2 2 0) orientation with weak intensity is also observed. The observed (2 0 0) orientation is in accordance with the reports on ion beam sputtered CdO films (Tanaka et al. (1969)). This indicates the crystalline nature strongly depends on substrate temperature. The lattice constant of the film is calculated from the interplanar spacing (d) value of the highest peak from the XRD pattern. The value of lattice constant is decreased from 0.4752 nm to 0.4694 nm with increase in temperature from room temperature (RT) to 350 °C.

The crystallite size (D) of Cr doped CdO thin films was calculated using Scherrer’s formula (Cullity (1978))
\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]

where \( \lambda \) is the X-ray wavelength (0.154 nm), \( \theta \) is the Bragg angle, and \( \beta \) is FWHM of (2 0 0) diffraction peak. The crystallite size increases from 28 nm to 42 nm with the increase of substrate temperature from RT to 350 °C. The structural parameters of Cr doped CdO films are given in Table 1. As the substrate temperature increases the adatom mobility also increases and the FWHM decreases from 0.926 nm to 0.804 nm which results in increase of crystallite size.

![XRD spectra of Cr doped CdO films deposited at different substrate temperatures.](image)

Table 1. Structural parameters of Cr doped CdO films.

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>2θ (degrees)</th>
<th>FWHM, ( \beta ) (degrees)</th>
<th>d-spacing (nm)</th>
<th>Lattice constant, ( a ) (nm)</th>
<th>Crystallite size, ( D ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>37.80</td>
<td>0.926</td>
<td>0.2376</td>
<td>0.4752</td>
<td>28</td>
</tr>
<tr>
<td>100</td>
<td>38.00</td>
<td>0.880</td>
<td>0.2370</td>
<td>0.4740</td>
<td>31</td>
</tr>
<tr>
<td>200</td>
<td>38.10</td>
<td>0.819</td>
<td>0.2362</td>
<td>0.4724</td>
<td>37</td>
</tr>
<tr>
<td>300</td>
<td>38.23</td>
<td>0.809</td>
<td>0.2354</td>
<td>0.4708</td>
<td>39</td>
</tr>
<tr>
<td>350</td>
<td>38.30</td>
<td>0.804</td>
<td>0.2347</td>
<td>0.4694</td>
<td>42</td>
</tr>
</tbody>
</table>

FESEM images of Cr doped CdO thin films deposited at various substrate temperatures are shown in Fig. 2. The films show an irregular surface morphology with higher roughness, and increased grain size can be evidenced with naked eye. The grain size obtained from FESEM image is found to be in the range of 30 – 48 nm. The relative compositions obtained from EDS for Cr doped CdO films deposited from RT to 350 °C are in an atomic ratio of Cd/O/Cr are 59.52/37.46/3.02%, 58.86/38.18/2.96%, 54.10/42.78/3.12%, 52.85/44.27/2.88% and 51.06 / 45.78 /3.16 %.
The electrical resistivity ($\rho$) of Cr doped CdO films were investigated by four-point probe method at room temperature. Fig. 3 shows the variation of the electrical resistivity of Cr doped CdO films as a function of the substrate temperature. The electrical properties of the films are highly influenced by the substrate temperature. The electrical resistivity decreased from $5.38 \times 10^{-4}$ to $1.92 \times 10^{-4}$ $\Omega$.cm with increase of substrate temperature from RT to 350 $^\circ$C. The decrease in resistivity with increase in substrate temperature is attributed to increase in grain size, reduction in grain boundary scattering and increased conductivity.
Fig. 4 shows the wavelength dependence of transmittance spectra of the Cr doped CdO films deposited at different substrate temperatures. The optical transmittance of Cr doped CdO film increases with the increase of substrate temperature. The optical absorption edge of the films shifted towards lower wavelengths with increase in the substrate temperature. The films deposited at substrate temperature 300 °C shows the highest optical transmittance of 85% and it is attributed due to less scattering effects, structural homogeneity, and better crystallinity. The optical absorption coefficient (α) evaluated from the transmittance spectra is in the range of (3 - 5.20) x 10^{-4} cm^{-1} at a wavelength of 600 nm.

The optical band gap, E_g is determined from the dependence of absorption coefficient values (α) on the photon energy, using Tauc’s relation (Tauc et al. (1966))

\[
(\alpha h\nu) = B(h\nu-E_g)^n
\]  

(2)

where B is a parameter that depends on the transition probability, E_g is the optical band gap energy of the material, h\nu is the photon energy and n is an index that characterizes the optical absorption process and is theoretically equal to 2 and ½ for indirect and direct allowed transitions respectively. The variation of \((\alpha h\nu)^2\) with photon energy (h\nu) of the films formed at different substrate temperature is shown in Fig. 5. The optical band gap of the films increased from 2.52 to 2.78 eV with increase in the substrate temperature from room temperature to 350 °C. The shift in absorption edge towards shorter wavelength suggests a widening of energy band gap with increasing substrate temperature and due to Burstein-Moss shift (Burstein (1954)).

![Fig. 4. Optical transmittance of Cr doped CdO films at different substrate temperatures.](image)

![Fig. 5. Plot of \((\alpha h\nu)^2\) with photon energy (h\nu) for Cr doped CdO films formed at different substrate temperatures.](image)
4. Conclusions

Cr doped CdO thin films were deposited on glass substrate by DC reactive magnetron sputtering at room temperature. XRD studies reveal that the films exhibit crystalline nature with preferred orientation along the (2 0 0) plane. The decrease in the electrical resistivity with the increase of the substrate temperature is due to the improvement in the degree of crystallinity of the films as revealed by the XRD. The minimum resistivity of $1.92 \times 10^{-4} \ \Omega \cdot \text{cm}$ and optical transmittance of 84% is obtained for the thin film deposited at 350 $^\circ \text{C}$ substrate temperature. The increase in optical band gap energy from 2.52 to 2.58 eV is attributed to Burstein-Moss effect. Our results suggest that the potential application of sputtered Cr doped CdO thin films can be used as transparent conducting oxide layer for different optoelectronic and photovoltaic devices.

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References