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Effect of film thickness on physical properties of DC reactive magnetron sputtered Cr doped CdO thin films

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Chromium doped CdO thin films have been prepared on glass substrates by DC reactive magnetron sputtering method. The prepared thin films have thickness varying from 250 to 400 nm and good adherence to the glass substrate. A systematic study has been made on structural, electrical and optical properties of Cr doped CdO thin films. XRD analysis showed that Cr doped CdO thin films exhibit cubic crystal structure with (2 0 0) preferred orientation. The electrical resistivity of the films decreases from 5.88 x 10^{-4} to 2.82 x 10^{-4} Ω.cm with the increase of film thickness. The average transmittance of Cr doped CdO films in the visible region was found to be in the range of 72-88% and the transmittance decreases with the increase of film thickness from 250 to 400 nm. The optical band gap value varies from 2.88 to 2.78 eV with increasing film thickness from 250 to 400 nm. The decrease of band gap with increase of film thickness could be due to the increase of density of localized states in the conduction band.

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1. Introduction

Transparent conducting oxides (TCOs) such as pure and doped indium oxide, zinc oxide, tin oxide and cadmium oxide have attracted much attention owing to their potential applications in opto-electronic device technology. In particular CdO based TCOs are of great interest due to their metal like charge transport behaviour with an exceptionally large carrier mobility and good optical transparency in the visible region [1-6]. CdO is an n-type semiconductor with non-stoichiometric composition due to the presence of either cadmium interstitials or oxygen vacancies, which acts as double charged donors [7]. Its high electrical conductivity and high optical transmittance in the visible region of the solar spectrum along with a moderate refractive index makes it useful for various applications such as photovoltaic solar cells, transparent electrodes, gas sensors, liquid crystal display, photodiodes, photo-transistors and optoelectronic devices [8-10].

CdO thin films have been prepared by different methods such as sol-gel [11], spray pyrolysis [12, 13], DC magnetron sputtering [14], chemical bath deposition (CBD) method [15], etc. Among these methods DC magnetron sputtering is presently the most commercial practiced method. Magnetron sputtering offers good control of the film composition because of high deposition rates. High deposition rates minimize the target poisoning effects during reactive sputtering. High energy of sputtered species, low pressure operation and low substrate temperature rise made magnetron sputtering an attractive technique to deposit films on different substrates. This article reports the effect of film thickness on structural, electrical and optical properties of chromium (Cr) doped CdO thin films by DC reactive magnetron sputtering technique.

2. Experimental details

Cr doped CdO thin films were prepared by DC reactive magnetron sputtering technique. 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 4 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. The depositions were carried out at room temperature with different thicknesses. Film thickness was measured by Talysurf thickness profilometer. The resulting thicknesses of the films are found to be in the range of 250- 400 nm. X-ray diffraction (XRD) patterns of the films were recorded with the help of Philips (PW 1830) X-ray diffractometer using CuKα radiation. The tube was operated at 30 KV, 20 mA with the scanning speed of 0.03(2θ)/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 resistivity of the films (ρ) was measured using the four-point probe method. Optical transmittance of the films was recorded as a function of wavelength in the range of 300 – 1200 nm using JASCO Model V-670 UV-Vis-NIR spectrophotometer (Japan).

3. Results and discussion

3.1 Structural properties

XRD patterns of Cr doped CdO thin films of different thickness are shown in Fig. 1. XRD patterns shows that the films exhibited predominantly a (2 0 0) orientation. The intensity of the diffraction peak (2 0 0) increases with the increase of film thickness from 250 to 400 nm. The full-width at half maximum (FWHM) decreases as the thickness of the film increases. The interplanar spacing (d) increases from 0.2337 to 0.2352 nm with the increase of film thickness (shown in Fig. 2). The evaluated lattice parameters from the XRD patterns were close to 0.468 nm (JCPDS No.05-0640) which is comparable to the bulk CdO ASTM data. The lattice constant values increases from 0.4674 to 0.4704 nm with the increase of film thickness. Since the radius (0.063 nm) of Cr^{3+} is smaller than that (0.095 nm) of Cd^{2+}, the increase in the lattice constants is probably due to the incorporation of Cr atoms are located at the interstitial site rather than Cd site. The structural parameters of Cr doped CdO thin films are given in Table 1.

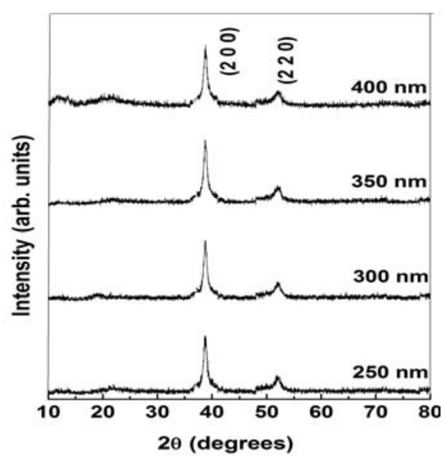

Fig. 1. XRD patterns of Cr doped CdO thin films with different thickness.

The crystallite size (D) of Cr doped CdO thin films was calculated using Scherrer's formula [16]

$$D=\frac{0.9\,\lambda}{\beta\cos\theta} \tag{1}$$

where λ is the X - ray wavelength (0.154 nm), θ is the Bragg angle, and β is FWHM of (2 0 0) diffraction peak. It is observed that the crystallite size increases from 23 to 38 nm with the increase of film thickness from 250 to 400 nm. The increase in the crystallite size may be caused by a columnar grain growth in the structure. The results reveal that the crystallization approaches more perfect as the film thickness was increased. The increasing in crystallite size with film thickness is in good agreement with previous reported results [17, 18].

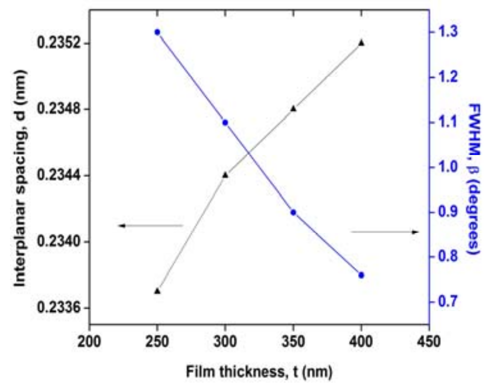

Fig. 2. Interplanar spacing (d) and FWHM (β) of Cr doped CdO thin films as a function of film thickness.

The dislocation density (δ) is defined as the length of dislocation lines per unit volume of crystal, it is evaluated using the formula

$$\delta = \frac{n}{D^2} \tag{2}$$

where n is a factor that equals unity when the dislocation density is minimum and D is the crystallite size. The microstrain is calculated from the relation

$$\varepsilon = \frac{\beta\cos\theta}{4} \tag{3}$$

The cumulative effect of the decrease in the microstrain and the dislocation density (shown in Table 1) can be used to explain the gradual reduction in the stacking fault probability of the films with increasing film thickness [19].

Table 1. Structural parameters of Cr doped CdO thin films with different thickness.

Film thickness, t (nm)	Crystallite size, D (nm)	Dislocation density, δ x 10^{15} (lines.m^{-2})	Strain, ε x 10^{-3} (lines^{-2}. m^{-4})
250	23	1.89	0.30
300	26	1.47	0.26
350	31	1.04	0.21
400	38	0.70	0.15

Fig. 3 shows Field emission scanning electron microscopy (FESEM) images of Cr doped CdO thin films deposited with different thickness. It is observed that the grain size increases from 18 to 42 nm with the increase of film thickness. FESEM image shows that the diffusion and transfer ability of surface atoms are improved with increasing film thickness, which leads to accelerated crystallization of the Cr doped CdO films and hence the enhancement of grain size. Fig. 4 shows EDS which gives the elemental composition of Cr doped CdO film of thickness 350 nm.

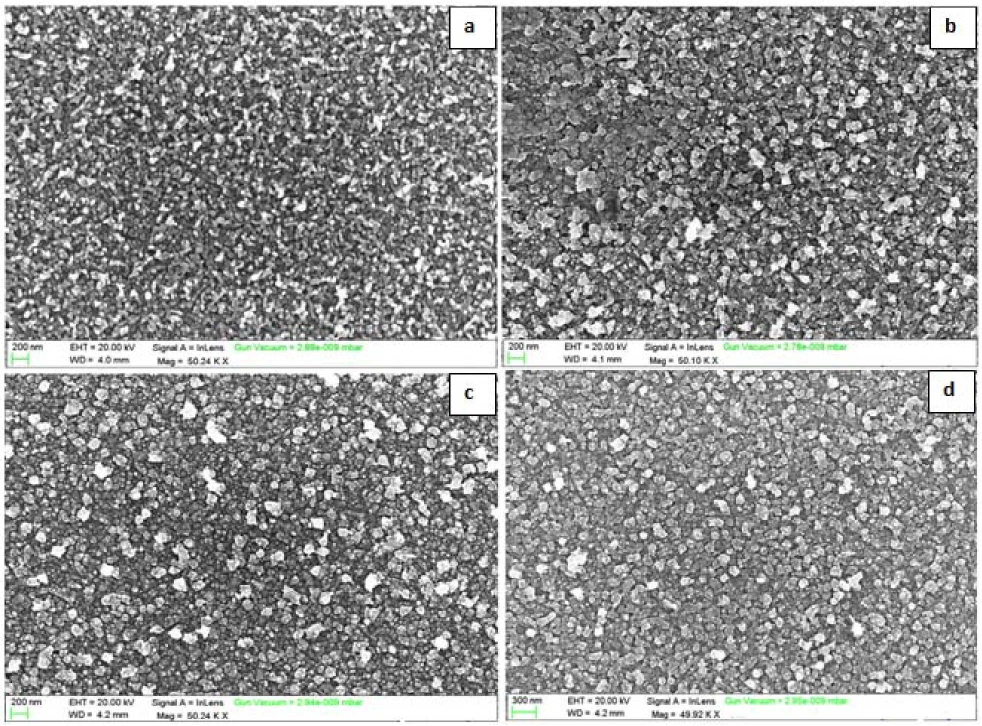

Fig. 3. FESEM images of Cr doped CdO thin films of various thicknesses (a) 250 nm, (b) 300 nm, (c) 350 nm and (d) 400 nm.

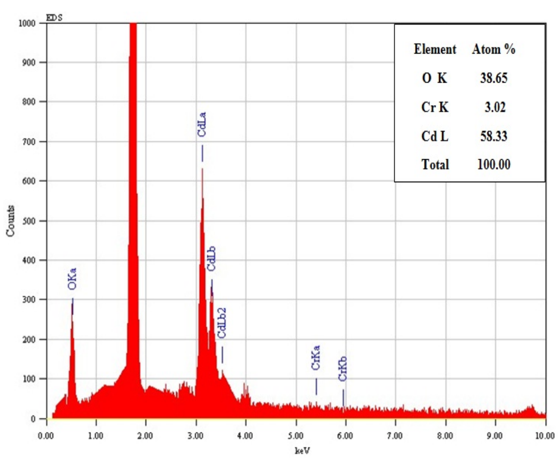

Fig. 4. EDS plot for Cr doped CdO thin film of thickness 350 nm.

3.2 Electrical properties

The high conductivity of the films mainly results from a non-stoichiometric composition or doping. Electrons in these films are supplied from donor sites associated with oxygen vacancies of high-valence metal ions. The electrical resistivity of the Cr doped CdO films were investigated by four-point probe method at room temperature. Fig. 5 shows the electrical resistivity of Cr doped CdO films as a function of film thickness. The resistivity values decreases from 5.88 x 10^{-4} to 2.82 x 10^{-4} Ω.cm with the increase of film thickness from 250 to 400 nm. The decrease in resistivity is probably due to the decrease in the number of grain boundaries with increased film thickness [20].

The sheet resistance (R_s) of Cr doped CdO thin films are calculated from the equation

$$R_s = \frac{\rho}{t} \quad \Omega/\text{sq} \qquad (4)$$

where ρ is resistivity and t is thickness of films.

The sheet resistance values for Cr doped CdO thin films with thickness 250, 300, 350 and 400 nm was found to be 23.6, 15.1, 8.5, 7.1 Ω/sq. The sheet resistance values decreases with the increase of film thickness from 250 to 400 nm. The observed values of the electrical parameters are comparable to the reported values on activated reactive evaporated [21] and magnetron sputtered [22] CdO films.

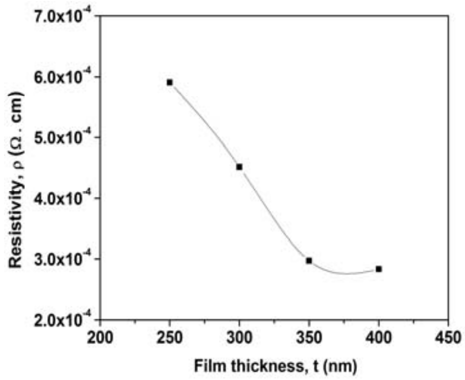

Fig. 5. Variation of electrical resistivity of Cr doped CdO thin films with different thickness.

3.3 Optical properties

Fig. 6 shows the optical transmittance spectra of Cr doped CdO thin films deposited with different thickness. The average transmittance of Cr doped CdO films with different thickness in the visible region were found to be in the range of 72-88%. The transmittance decreases with the increase of film thickness owing to some displacement of the absorption edge towards higher wavelengths that can be observed in the transmittance spectra.

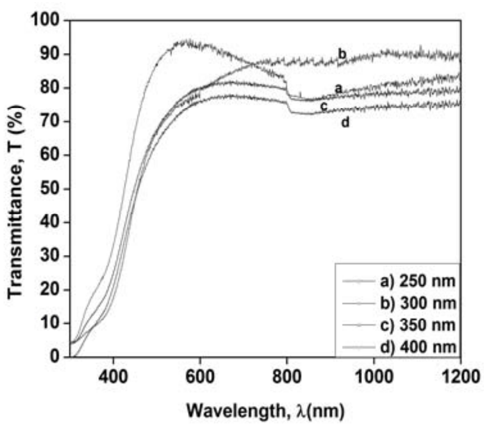

Fig. 6. Optical transmittance spectra of Cr doped CdO thin films of various thicknesses.

From the transmittance data, the absorption coefficient (α) of the film was determined using the relation [23],

$$\alpha = \frac{\ln\left(\frac{1}{T}\right)}{t} \qquad (5)$$

where T is film transmittance and t is the thickness of the film. The optical absorption coefficient (α) evaluated from the transmittance data is in the range of (2 – 6.3) x $10^4 cm^{-1}$. The absorption coefficient increases with the thickness of the film strongly demonstrating that the film property is thickness dependent.

The optical band gap of the Cr doped CdO films can be determined using optical absorption method. In this method, the relation between absorption coefficient and photon energy is expressed by the following equation [24]

$$(\alpha h\nu) = B\,(h\nu - E_g)^n \qquad (6)$$

where B is a parameter that depends on the transition probability E_g is the optical band gap energy of the material, hυ 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.

For evaluating the optical band gap of Cr doped CdO films $(\alpha h\upsilon)^2$ is plotted versus photon energy as shown in Fig. 7. The optical band gap decreases from 2.88 to 2.78 eV with increasing film thickness because crystal defects can be formed which produce localized states that change the defective Fermi level due to an increase in carrier concentrations [25]. Also the decrease of direct band gap with the increase of thickness can be attributed to increase of density of localized states in the conduction band.

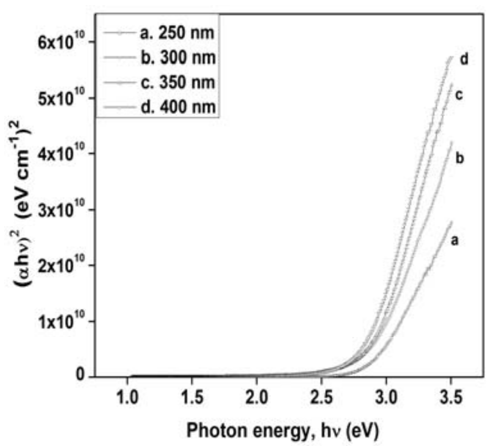

Fig. 7. Variation of $(\alpha h\nu)^2$ versus photon energy hν of Cr doped CdO thin films with different thickness.

Optical transmittance and the electrical conductivity are two important parameters with which the quality of the TCOs is judged. The film quality was determined from figure of merit (□) calculated by using the formula given by Haacke [26].

$$\phi = \frac{T^{10}}{R_s} \quad \Omega^{-1} \qquad (7)$$

where T is the film average optical transmittance in visible region and R_s is the sheet resistance. A film with low electrical resistivity and high optical transmittance would have a relatively high figure of merit. The figure of merit for the film thickness 250, 300, 350 and 400 nm is found to be 1.24 x 10^{-2} Ω^{-1}, 1.88 x 10^{-2} Ω^{-1}, 5.14 x 10^{-2} Ω^{-1} and 6.14 x 10^{-2} Ω^{-1}. The highest value of figure of merit was 6.14 x 10^{-2} Ω^{-1} for the film with thickness 400 nm.

4. Conclusion

Cr doped CdO thin films were deposited on glass substrate by DC reactive magnetron sputtering with different thickness. 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 film thickness is due to the improvement in the degree of crystallinity of the films as revealed by the XRD. The average optical transmittance of the films decreases with increase of film thickness owing to some displacement of the absorption edge towards higher wavelengths. The high value of figure of merit of Cr doped CdO film with thickness 400 nm could find extensive applications in large area optoelectronic devices.

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