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Studies on sputtered ZnO:CdO thin films for TCO application

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Abstract. Zinc oxide (ZnO) and cadmium oxide (CdO) thin films were studied for their electrical and optical properties for transparent conducing oxides (TCO) application. Using zinc (Zn) and cadmium (Cd) as targets, ZnO and CdO thin films were deposited and also ZnO:CdO thin film samples were co-deposited on to the glass substrates by reactive direct current (DC) magnetron sputtering. X-ray diffraction (XRD patterns of ZnO and CdO films showed the diffraction planes corresponding to ZnO (002) and CdO (200) respectively. The optical band gap of the films varied between 2.5 – 3.2 eV as determined by UV-VIS spectrophotometry. The films exhibited Ohmic behaviour.

1. Introduction

TCOs are an excellent class of materials which merge both high optical transparency and high electrical conductivity. To have this physical properties, material should have sufficiently large energy band gap so that it is transparent to visible light or not absorbing, with conductivity, an electron or hole concentration with a sufficiently larger mobility. Glass fibres are transparent but are electrical insulators on the other hand compound semiconductors are dopant dependent for their electrical conductivity. And thus TCO's have to obtain a midway between both these properties where the conductivity has to be that of close to a metal as well as with high transparency [1, 3]. Binary and ternary compounds such as SnO_2, ZnO, In_2O_3, Ga_2O_3, CdO, Cd_2SnO_4, $CdSnO_3$, $CdIn_2O_4$ and Zn_2SnO_4 are well known TCOs/are currently used in TCO application. Among those materials ZnO and CdO are well known for their tunable optical and electrical property which helps in obtaining large energy bandgap and high mobility. ZnO is an n-type semiconductor with a band gap value of ~3.3 eV at room temperature. Some of the important and attractive properties of ZnO are having very good transparency, fast electron mobility and strong room-temperature luminescence. ZnO is employed in several applications such as transparent electrodes in opto-electronic devices like liquid crystal displays, organic light emitting diodes, solar energy cell, smart windows and electronics as both active and passive devices like diodes, thin film transistors, etc. CdO is an n-type semiconductor with a band gap value of ~ 2.18 to 2.31 eV at room temperature. Nanostructured CdO is used as TCO materials for its higher conductivity. The CdO thin films has been used in wide range of applications, such as, photodiodes, phototransistors, photovoltaic cells, transparent conducting electrodes, liquid crystal displays, light detectors and reflectors [4, 5]. ZnO:CdO thin films can be produced by various methods like sol-gel spin coating method, spray pyrolysis, LPCVD, extraction-pyrolytic method, etc., ZnO-CdO composite thin films are generally prepared by various physical and chemical deposition techniques, like electro-deposition [6], radio frequency magnetron sputtering [7], molecular beam epitaxy [8], sol–gel process [9], chemical vapour deposition [10] and spray pyrolysis [11]. The main advantage of preparing thin films by sputtering is to achieve smooth films which are

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highly useful at the interface of the layers of the TCO. The present work focuses on the co-deposition of ZnO:CdO to enhance the TCO properties (optical transparency and Ohmic behaviour)

2. Experimental details

ZnO, CdO and ZnO: CdO films were prepared by reactive DC magnetron sputtering technique at room temperature. Zn and Cd targets (purity 99.999 %, 2' dia: 3.2 mm thickness) were used as source materials for depositing ZnO and CdO thin films. Thoroughly cleaned borosilicate glass substrates of dimension 2×1 cm^2 were used for depositions. Cleaning procedure for glass substrates is given as follows: initially substrates were cleaned using Triton-X to remove viscous residues and then rinsed thoroughly in running water followed by double distilled water. The rinsed substrates were ultrasonically agitated in acetone and ethanol for five minutes in each solution and then dried in hot air oven. Cleaned substrates were placed in the substrate table and the deposition chamber was evacuated to the base pressure of 3.5×10^{-5} mbar. Argon (Ar) and oxygen (O_2) were used as sputtering and reactive gas respectively. ZnO films were prepared by keeping cathode power as 30 W and deposition duration of 5 min. CdO thin films were prepared by keeping cathode power 40 W and deposition time 5 min. ZnO:CdO deposition was carried out for 5 min with cathode power of 40 W under Ar:O_2 partial pressure of about 1:3.5 at room temperature. The thickness value of the films were measured using stylus probe profilometer (Mitutoyo 201) and the thickness values of the deposited films were 300,335 and 350 nm for the ZnO and (CdO, ZnO:CdO) thin films deposited at 30 W and 40 W respectively. XRD measurements were done by Bruker D8 focus diffractometer with Cu K_α radiation (wavelength 1.54 Å) to investigate the crystal structure. The optical absorbance spectra and Tau's plot were collected using a UV–Vis spectrophotometer (Perkin Elmer, Lambda 950).The current-voltage characteristics were measured with a Keithley 4200 semiconductor characterization system.

3. Results and discussions

3.1. X-ray diffraction analysis

The crystalline properties and material phases of the ZnO, CdO and ZnO:CdO thin films were studied structurally by means of XRD measurements in the scan range of 30º–80º which are shown in Fig 1. The pure ZnO thin film exhibited the hexagonal wurtzite structure (JCPDS: 01-075-1256) while CdO thin film had the cubic structure (JCPDS: 01-075-2245).For both ZnO and CdO compounds, mixed crystallite phases of with hexagonal and cubic structures were found. This was due to the larger ionic radius of Cd compared to Zn: the small amount of CdO in the ZnO making up sample ZnO:CdO caused a lattice expansion and hence a shift to smaller 2θ angles. The clear presence of mixed crystallite phases of both ZnO and CdO compound was found with hexagonal and cubic structures, respectively [10-12].

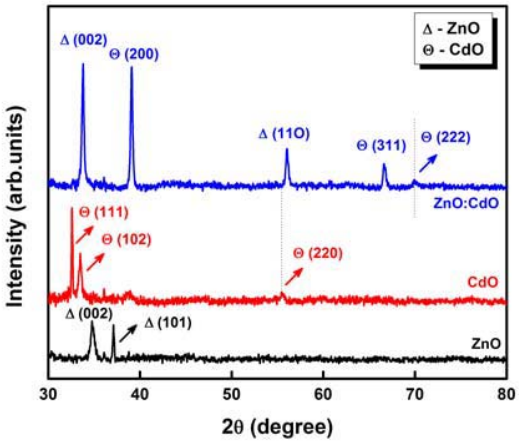


Figure 1. XRD patterns of ZnO, CdO, ZnO:CdO thin films

3.2. Optical analysis

The optical properties were studied for ZnO, CdO and ZnO:CdO thin films. Fig 2. showed the absorbance spectra in the wavelength range 300–800 nm respectively. The absorbance increased as the CdO concentration increased in the films. The transmittance is decreased with the doping of CdO in the samples and it might be due to band-to-band absorption of the CdO with its bandgap smaller than that of ZnO or due to the increased optical scattering of incident light on the film surface [11, 13].

The dependence of the absorption coefficient with the photon energies fitted to the relationship for the allowed direct transition [14]

$$(\alpha h\nu)^2 = B(h\nu - E_g) \quad (1)$$

where, B is a constant. By extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ vs. hν shown in Fig 3. The optical bandgap Eg values were obtained. With the doping of Cd, the optical bandgap increased. The optical absorption edge was blue shifted with the doping of Cd from ZnO to CdO [15].

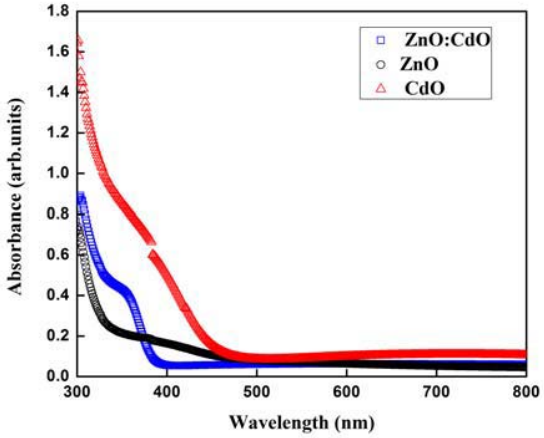


Figure 2. Absorbance spectra of ZnO, CdO, ZnO:CdO thin films

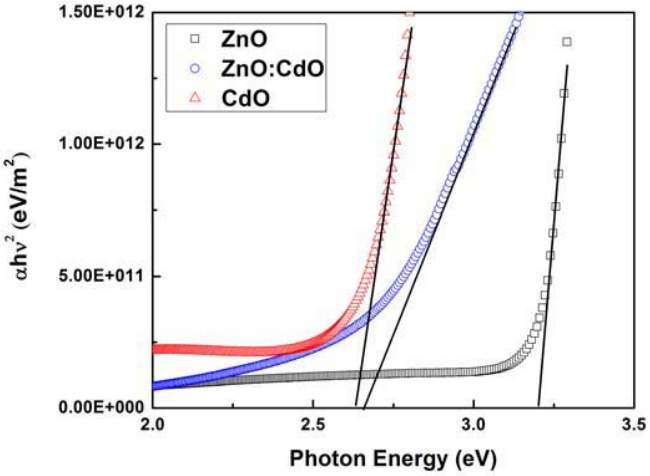


Figure 3. Tau's plot of ZnO, CdO, ZnO:CdO thin films

3.3. Electrical studies

The electrical characterization of the ZnO, CdO and ZnO-CdO thin films was carried out by using Keithley 4200 semiconductor characterization system. After making contacts with aluminum foil, the variation of current with voltage was noted between -10 and 10 V at room temperature and room lighting for all samples and is shown in Figs. 4, 5 and 6. The Ohmic conduction mechanism was observed for ZnO:CdO films and they had low resistivity compared to the other samples (ZnO and CdO), for which there was a deviation from Ohmic behavior, together with higher resistivity. It was observed that the ZnO rich thin film has a high resistivity, due to grain boundary effects and also, due to the semiconducting nature of the ZnO, which will create a potential barrier that affects the electrical transport causing a reduction in conductivity [16]. With the addition of cadium oxide to Zinc oxide, the resistivity has decreased as observed. This interpretation is consistent with the optical measurements where a decrease in band gap with the co-deposition of ZnO:CdO occurred. The Cd proportion therefore plays an important role in the electrical characteristics.

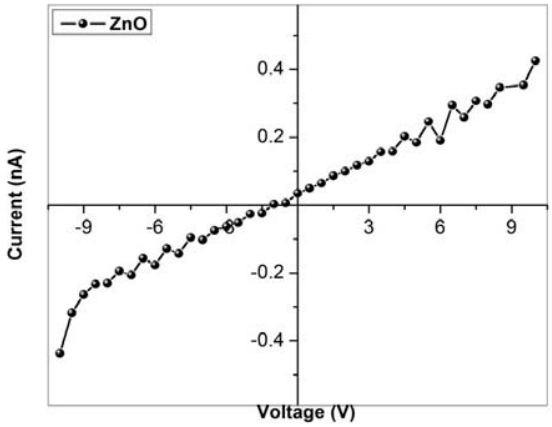


Figure 4. I-V curve of ZnO thin film

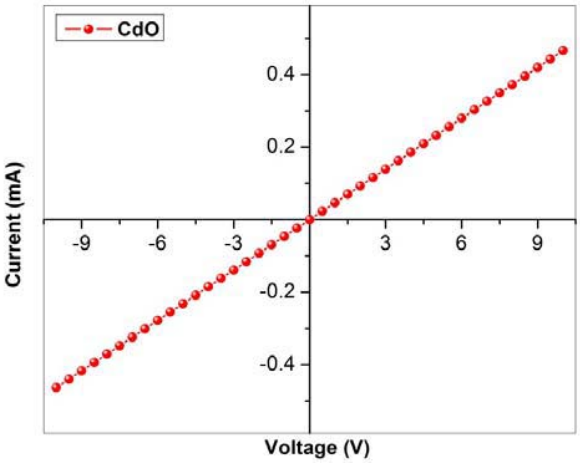


Figure 5. I-V curve of CdO thin film

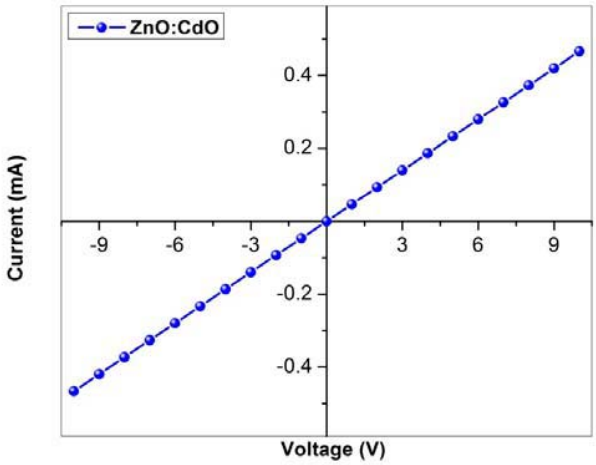


Figure 6. I-V curve of ZnO:CdO thin film

Mixed oxides of ZnO:CdO thin films were successfully deposited using the sputtering method. The XRD diffraction results showed that the polycrystalline nature of the thin films changed from the hexagonal structure characteristic of ZnO to a cubic structure characteristic of CdO for the thin films containing a high concentration of ZnO to the films containing a high concentration of CdO, with no smooth transition. From the optical analysis, it was found have high transparency in the visible region. From the electrical studies, it was observed that with the addition of cadium oxide to Zinc oxide, the resistivity has decreased. These highly conducting and low optical band gap thin films may be suitable for applications in solar cells and optoelectronic devices.

4. Conclusion

ZnO:CdO thin films were deposited on glass substrates by dc magnetron sputtering .The structural, optical and electrical properties of the films were studied from the view of their application as transparent electrodes. It was observed from the XRD that the polycrystalline nature of the thin films. An improvement in crystallinity with the addition of CdO was also observed. From the optical analysis, it was found that the transmittance and band gap of the sample decreased with an increasing CdO concentration. From the electrical studies, it was found that the resistivity of the mixed oxide thin films decreased with the addition of CdO proportion.

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6. Author Contributions

This paper is based mainly on the M. Tech. project report of V Maragatham, for which M. Sridharan served as supervisor. VM performed the majority of the experiments, analysis and interpretation and wrote the paper based on her project report. V Sushmitha and P Deepak Raj contributed to the planning of the experiments and interpretation. All coauthors read and commented on the manuscript.

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