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Preparation and Characterization of Highly Conducting and Optically Transparent Fluorine Doped CdO Thin Films

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Abstract: A highly transparent and conducting metal oxide (TCO) film is a compromise between low resistivity and high transmittance. In the present study, fluorine doped cadmium oxide thin films (F:CdO) as TCO film were prepared with low sheet resistance (4 Ω cm^{-2}) and high optical transmittance (85%). F:CdO films were deposited using spray pyrolysis method with precursor concentration of 0.1 M Cadmium acetate doped with 0.002, 0.004 and 0.006 M concentration of ammonium fluoride. Substrate temperature was fixed at 250°C with precursor solution flow rate of 3 mL min^{-1}. The structural, morphological, optical and electrical characterization of F:CdO were investigated using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), UV-visible spectrometer and four probe method, respectively. The structural studies confirms the polycrystalline nature of film with preferential orientation along (111) plane. Morphological studies show the presence of closely packed spherical grains. The band gap obtained by optical studies was found to vary between 2.5-2.8 eV for increasing fluorine concentration. The transparence of the film is found to be high in the range of 85%. Variation of electrical and optical parameters as a function of fluorine concentration were analyzed and reported.

Key words: Transparent conducting oxide, spray pyrolysis, CdO, parameters, fluorine concentration

INTRODUCTION

Transparent Conducting Oxides (TCO) thin films such as Indium Zinc Oxide (IZO), Aluminum Zinc Oxide (AZO), Gallium Zinc Oxide (GZO) Indium Tin Oxide (ITO), were prepared by various technique like spray pyrolysis, sputtering, reactive sputtering, sol-gel, MOCVD, PLD, etc. Cadmium oxide (CdO), tin oxide (SnO_2) and zinc oxide (ZnO) have attracted researchers due to their promising perspectives for variety of application in optoelectronics and photovoltaic devices. TCO have high electrical conductivity and optical transmission properties that finds variety of applications in anti-reflection coatings (Fleischer *et al*., 2012), IR detectors (Kolahdouz *et al*., 2011), liquid crystal displays (Ma *et al*., 2011), photodiodes (Yuan *et al*., 2012), photovoltaic cell (Fleischer *et al*., 2012), gas sensors (Rambu *et al*., 2011) and Organic Light Emitting Diodes (OLEDs) (Vaufrey *et al*., 2002) etc.

In particular, fluorine doped CdO is a promising TCO material due to its high electrical conductivity and optical transmittance in the visible region of electromagnetic spectrum (Hitosugi *et al*., 2009). Undoped CdO films shows low resistivity and studies were made to decrease the resistivity even more and getting the stable thin film. The CdO thin films have energy band gap between 2.3-2.9 eV which has good optical transmission. The presence of CdO interstitial atoms and oxygen vacancies act as double donors which shows n-type behavior. CdO have been doped with many elements such as In, Sn, F, etc., but the fluorine is chosen because they are less expensive and less toxic. F:CdO thin films were deposited using Spray pyrolysis method. Spray pyrolysis method have the advantage of formation of fine grains, chemically homogeneous nano structured film. The CdO films are annealed at different temperature to increase the conductivity of the sample. In this study, we are reporting the effect of fluorine concentration on CdO film with structural, optical and electrical properties of thin films grown by spray pyrolysis technique.

MATERIALS AND METHODS

Fluorine doped cadmium oxide thin films were deposited on the glass substrate from aqueous solution of cadmium acetate [$Cd(CH_3COO)_2.2H_2O$] with a

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concentration of 0.1 M dissolved in 50 mL of deionized water. For doping with fluorine different concentration 0.002, 0.004 and 0.006 M of ammonium fluoride was dissolved in deionized water of 50 mL and both are mixed together to form a 100 mL solution. The high quality thin films were deposited using a home built spraying system. Spray gun consists of inner nozzle of tip diameter 0.52 mm which is connected to precursor solution and outer nozzle of 0.78 mm is connected to air compressor. Prior to spraying the precursor solution on to the glass substrates, they were chemically cleaned and dried. The precursor solution is sprayed to the preheated glass substrate kept at a temperature of 230°C. In order to maintain a constant temperature of 230°C during spraying process the electric plate is connected to a digital thermostat. The precursor solution was sprayed at an angle of 45° with respect to glass substrate to nozzle tip which is kept at a distance of 50 cm from spray gun. Compressed air is used as carrier gas which is kept at a pressure of 2 kg cm^{-2} from air compressor through air filter and regulator to get a fine mist of spray. The solution spray rate is maintained at 3 mL min^{-1}, between successive spray, a time period of 15 sec was allowed to avoid excessive cooling of substrate. A chrome-nickel thermocouple was used to control substrate temperature with an accuracy of 2°C. Large number of fluorine doped CdO thin films were deposited to optimize the nanocrystalline film. The structural studies of the films were carried out using PANalytical X-ray diffractometer using Ni-filtered CuKa radiation (λ = 1.5406 Å), was employed with generator setting of 40 kV and 30 mA. A scanning speed of 10° min^{-1} is maintained in continuous scan. X-ray line broadening was adopted to determine microstructural details. Surface morphology of film were studied using HITACHI Scanning Electron Microscope (Model S-3000H) with an accelerating potential of 18 kV. Optical studies were carried out using Perkin-Elmer Lambda-2 Spectrometer, in the 300-1100 nm wavelength range. The transmission was measured using glass as a reference. A simple, nondestructive way of determining ρ utilizes the four probe method. Four sharp tipped tungsten wires (tungsten is chosen for its hardness) are brought into contact with the film surface. The four point probe avoids contact error problem by using a row of four equally spaced contacts. The current-voltage(I-V) characteristics and resistance temperature studies were taken by four probe method.

Structural characterization: X-ray diffraction pattern of a representative F:CdO film using Cu Ka radiation (λ = 1.5406 Å) is shown in Fig. 1. The XRD pattern of undoped CdO and fluorine doped CdO films prepared by spray pyrolysis with the precursor concentration 0.1 M of cadmium acetate with 0.002, 0.004 and 0.006 M ammonium fluoride. The obtained XRD pattern is compared with JCPDS card [05-0640] indicating polycrystalline nature with face centered cubic crystal structure. The random growth of film is due to amorphous nature of the substrate. The planes are indexed as (111), (200), (220), (311) and (222) with respect to standard card. XRD lines shows broadened in their shape when compared with standard JCPDS line. The preferential growth is along (111) plane is observed for undoped CdO films and fluorine doped CdO films. The preferential orientation changes from (111) plane to (200) plane for higher concentration of fluorine at 0.006 M. These XRD patterns do not show the presence of any fluorine compound, even though the films are doped with fluorine.

The grain size for the different fluorine concentrations was calculated using the Full-Width at Half-Maximum (FWHM) of the peaks. The Scherrer's formula (Hindeleh and Johnson, 1980) is utilized to determine grain size from the line broadening effect. The FWHM (β) can be expressed as a linear combination of the grain size (D) through the following relation:

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where, D is the size of the grain in the direction perpendicular to the reflecting planes, θ is the diffraction angle, K is the shape factor and is equal to 0.9, λ is the wavelength of X-ray and β the full width at half maximum of prominent peaks in radian.

It was found that grain size varies from 35 to 40 nm as precursor concentration increased from 0.002 to 0.006 M of ammonium fluoride with 0.1 M of cadmium acetate. The fluorine doping heals the materials by filling the oxygen vacancies with F atoms.

Morphological studies: Surface morphology of the films was investigated by using HITACHI Scanning Electron Microscope (Model S-3000H) with an accelerating potential of 18 kV. Prior to imaging, the films were sputtered with thin gold film to enhance the emission of secondary electron for better imaging. Figure 2 shows the surface morphology of F:CdO thin film prepared from the optimized condition. The film has porous with grains composed of smaller crystallites.

It shows the F:CdO deposited on glass substrate was grown as spherical shape grains like morphology. Each grain can be indexed to have cubic crystalline nature. Also, the image shows the presence of void between grains. This may decrease the electron conductivity

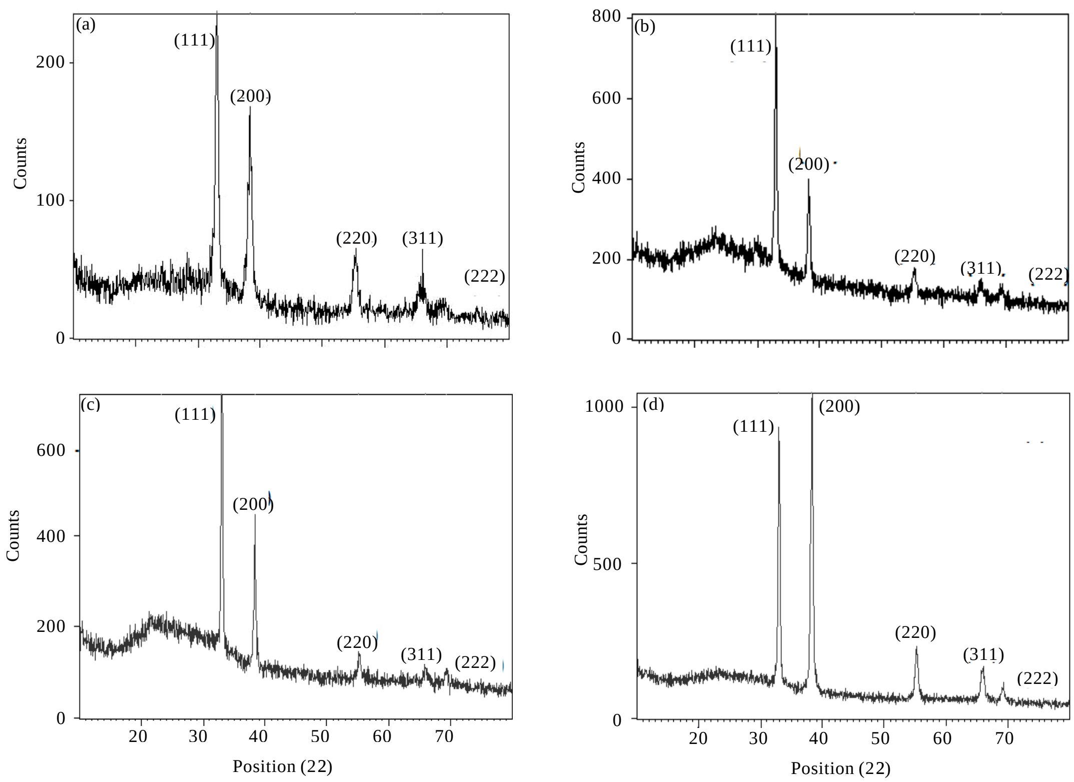

Fig. 1(a-d): XRD pattern of 0.1 M of cadmium acetate with various fluorine concentration; (a) Undoped CdO, (b) 0.002 M fluorine doped CdO, (c) 0.004 M fluorine doped CdO and (d) 0.006 M fluorine doped CdO

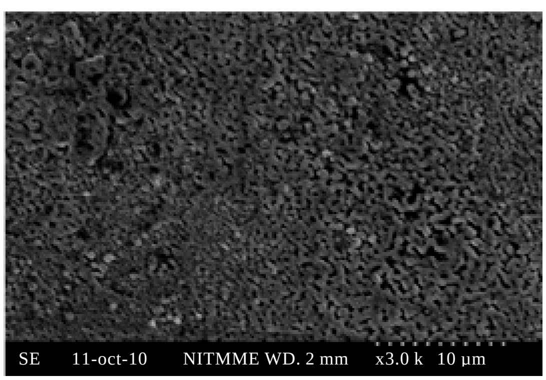

Fig. 2: Scanning electron microscope image of fluorine doped CdO on glass substrate

between grains. However, the film resistance obtained from high impedance meter show 8 Ω cm^{-2}. This indicates film below the surface were porous free and only the surface state with porous structure.

Optical characterization: Figure 3a-c show optical absorbance and transmittance of F:CdO film prepared at optimized condition. It shows a smooth increase in transmission above 600 nm. This smooth increase is due to crystalline nature of the prepared film. The maximum transmission found to be 90% at 800 nm. The absorption coefficient α is calculated from Lambert's law:

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

where 'A' is optical absorbance and 't' is the film thickness obtained from loss of weight method (Akyuz *et al*., 2011).

The transmission of the film is more than 87% and the presence of fluorine does not decrease the transmission. The doping of fluorine results in the shift of edge towards lower wavelength for increase in fluorine content. From the plot between $(\alpha h\nu)^2$ and hν as shown in Fig. 4 direct allowed band gap were determined.

The optical band gaps calculated were not exact band gaps, in the degenerate semiconductors, the Fermi level lies well within the conduction band and its position depends on the free electron density. The optical band gap is the gap between the valence band and conduction

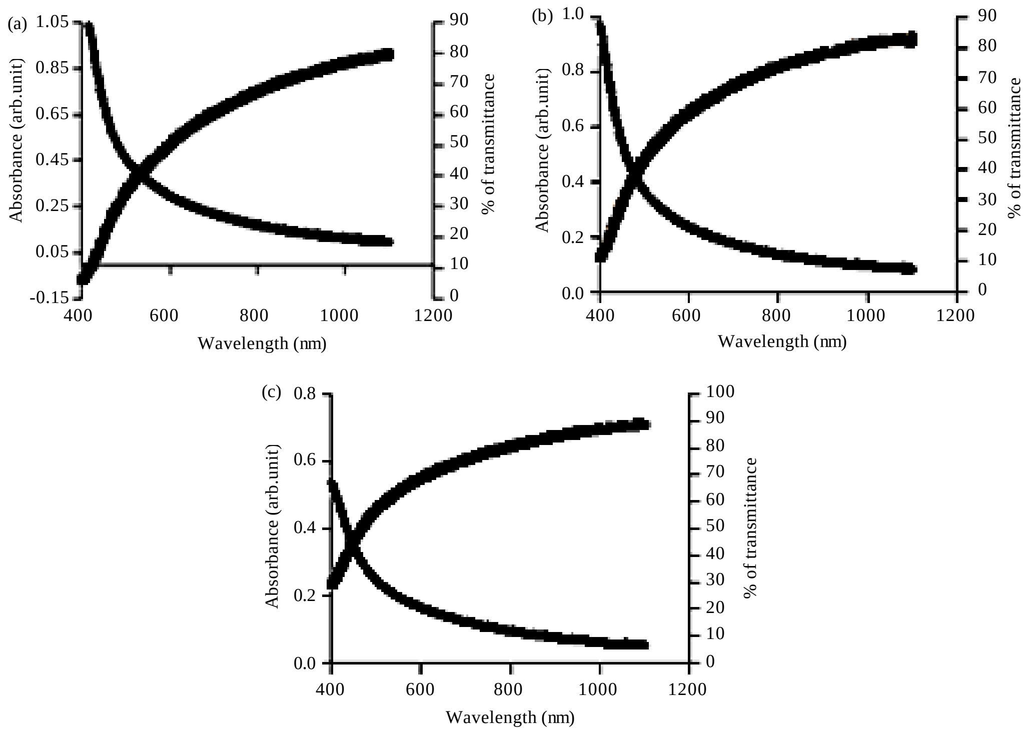

Fig. 3(a-c): Optical absorbance and transmission of 0.1 M cadmium acetate with fluorine concentration; (a) 0.002 M, (b) 0.004 M and (c) 0.006 M

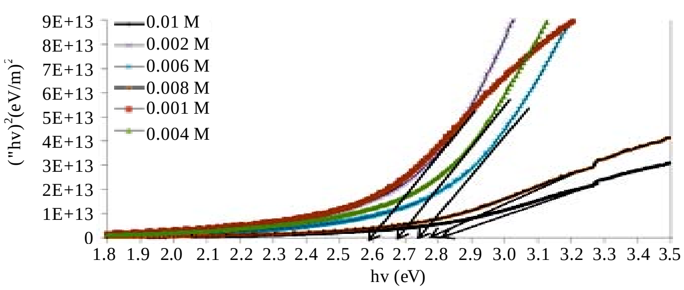

Fig. 4: $(\alpha h\nu)^2$ vs. hν and the variation of the optical band gap for the 0.1 M cadmium acetate with at various concentration of ammonium fluoride samples

band, whereas here they are related to the excitation of electrons from valence band to the Fermi energy level in conduction band concentration; 0.002, 0.004 and 0.006 M.

The increase in the fluorine concentration results in the sharp increase of optical band gap. With fluorine doping the shift in the absorption is clearly seen in Fig. 4. The lifting of Fermi energy level well in the conduction band of degenerate semiconductors is due to increase in the carrier concentration which leads to the energy band broadening effect. This effect is called as Moss-Burstein effect which effects the increase in band gap due to increase in fluorine concentration. The graph is extrapolated to give E_g value and the value is found to be 2.50-2.80 eV and agrees with the literature report (Kul *et al*., 2007).

CHARACTERIZATION

The resistivity (ρ) of the films with different fluorine concentrations was measured at various temperatures (T) between 0 to 250°C. Figure 5 shows the graph of

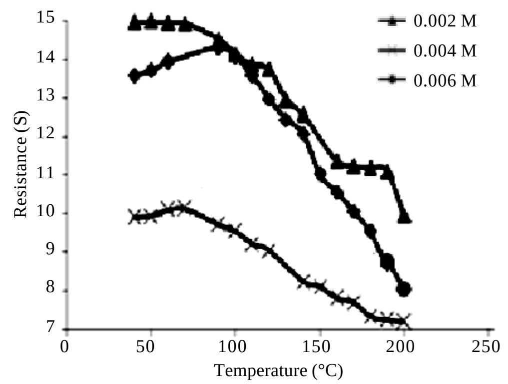

Fig. 5: Resistance vs. temperature plot for different fluorine concentration in CdO film

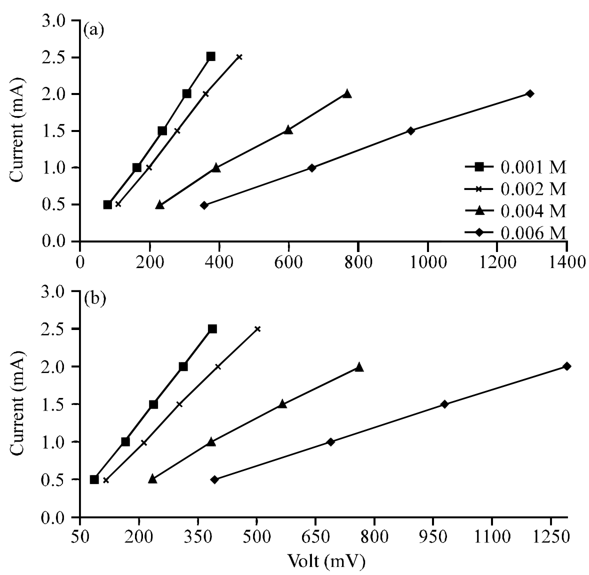

Fig. 6(a-b): Current vs. voltage plot of different fluorine concentration in CdO film at (a) 40°C and (b) 70°C

resistivity (ρ) vs. temperature (T) for different Fluorine concentrations. The result shows a decrease in resistivity with increase in temperature which obeys negative temperature coefficient as seen in semiconductors (Ghosh *et al*., 2005). There is a tremendous decrease of resistivity after 150°C which shows the negative temperature coefficient of resistance that observed in semiconductor.

From Fig. 5 it is seen at low temperature of 40°C the resistance is 11 Ω cm^{-2}, at high temperature of 200°C resistance drops to 8 Ω cm^{-2} which clearly gives the information of negative temperature coefficient of direct band fluorine doped CdO films.

From Fig. 6, I-V characteristics shows that the concentration increases from 0.002 to 0.006 M doping of fluorine the conductivity seems to increase and current increases linearly with applied voltage for various concentration as seen in the. Figure 6 for different temperatures (a) 40°C and (b) 70°C. The current increases linearly to the applied voltage which obeys Ohm's law.

CONCLUSION

Undoped and fluorine doped CdO thin film have been deposited using spray pyrolysis technique. X-ray diffraction studies show that all the films were polycrystalline with cubic crystal structure and preferential orientation along (111) plane. No significant change is observed in crystal structure due to fluorine doping. The SEM results show the presence of spherical shaped grains. Optical studies show a good transparency in the visible region. The transparency found to increases up to 90% as fluorine concentration increases in CdO film. Also band gap vary from 2.50-2.80 eV as fluorine concentration increases in CdO films. The sheet resistance of the films was obtained using four probe method and it is found to vary between 4-8 Ω cm^{-1}, respectively with an increase in fluorine concentrations in CdO film. Hence the increasing of fluorine concentration, results in increase of optical transparency but decrease in electrical conductivity. However, optimum concentration of fluorine doping (0.006 M) found to have better conductivity and optical transparency (87%). Thus, at this fluorine concentration in CdO gives good TCO property.

REFERENCES

Akyuz, I., S. Kose, E. Ketenci, V. Bilgin and F. Atay, 2011. Optical, structural and surface characterization of ultrasonically sprayed CdO: F films. J. Alloys Compd., 509: 1947-1952.

Fleischer, K., E. Arca and I.V. Shvets, 2012. Improving solar cell efficiency with optically optimised TCO layers. Sol. Energy Mater. Sol. Cells, 101: 262-269.

Ghosh, P.K., S. Das, S. Kundoo and K.K. Chattopadhyay, 2005. Effect of fluorine doping on semiconductor to metal-like transition and optical properties of cadmium oxide thin films deposited by sol-gel process. J. Sol-Gel Sci. Technol., 34: 173-179.

Hindeleh, A.M. and D.J. Johnson, 1980. An empirical estimation of Scherrer parameters for the evaluation of true crystallite size in fibrous polymers. Polymer., 21: 929-935.

Hitosugi, T., N. Yamada, N.L.H. Hoang, J. Kasai, S. Nakao, T. Shimada and T. Hasegawa, 2009. Fabrication of TiO_2-based transparent conducting oxide on glass and polyimide substrates. Thin Solid Films., 517: 3106-3109.

Kolahdouz, M., A. Afshar Farniya, M. Ostling and H.H. Radamson, 2011. The performance improvement evaluation for SiGe-based IR detectors. Solid-State Electron., 62: 72-76.

Kul, M., M. Zor, A.S. Aybek, S. Irmak and E.T.M. Kul *et al*., 2007. Some structural properties of CdO:F films produced by ultrasonic spray pyrolysis method. Thin Solid Films, 515: 8590-8593.

Ma, J., X. Ye and B. Jin, 2011. Structure and application of polarizer film for thin-film-transistor liquid crystal displays. Displays., 32: 49-57.

Rambu, A.P., D. Sirbu, N. Iftimie and G.I. Rusu, 2011. Polycrystalline ZnO-In_2O_3 thin films as gas sensors. Thin Solid Films, 520: 1303-1307.

Vaufrey, D., M.B. Khalifa, M.P. Besland, J. Tardy and C. Sandu *et al*., 2002. Electrical and optical characteristics of indium tin oxide thin films deposited by cathodic sputtering for top emitting organic electroluminescent devices. Mater. Sci. Eng., C., 21: 265-271.

Yuan, Z., J. Yu, N. Wang and Y. Jiang, 2012. A hybrid photodiode with planar heterojunction structure consisting of ZnO nanoparticles and CuPc thin film. Curr. Appl. Phys., 12: 1-5.