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Research Paper

CONSEQUENCE OF PURE AND Cu & Zn DOPED CdO THIN FILMS USING SPRAY PYROLYSIS TECHNIQUE

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Abstract

In this work Pure (undoped) and Zinc, Copper (Cu) doped CdO thin films are prepared using spray pyrolysis technique on glass substrates. Influence of Zn & Cu doping on the structural, optical and electrical properties of CdO thin films were reported. XRD analysis reveals that the prepared pure and Zn & Cu doped CdO films show polycrystalline nature with face centered cubic (FCC) structure. Also, Zn& Cu doping significantly increases the crystalline and changes the crystallite size. SEM images shows grains which are uniform and spherical shaped grains. The transmittance of the prepared CdO films recorded in the UV visible spectra show 40 to 70% in the visible region. The estimated optical band gap values are blue shifted in Zn doped CdO thin films. Hall measurement shows that the films are N-type semiconductor. Also, it is observed that when the Cu doped, the electrical resistivity is high when compared to Zn doped CdO thin films.

Keywords: *Spray Pyrolysis, UV Visible, FCC, N-type Semiconductor.*

1. INTRODUCTION

During the last few decades, transparent conducting oxides have become important materials, with numerous publications focusing on different types of these materials, such as:ZnO and CdO. Recently, there has been growing interest in the use of CdO.CdO is one of the first examples of TCO materials reported by Badeker in 1907. It is an N-type semiconductor with a rock-salt crystal structure and possesses a direct gap of 2.2 eV**(Kumaravel et al., 2010)**.The material exhibits a high electrical conductivity and the reported resistivity value vary from 10-2 to 10-4 Ωcm based on the addition of dopants and the level of doping concentration. The review article on CdO **(Chandiramouli & Jeyaprakash, 2013)** suggests that the number of publications dramatically increased from 2005 onwards due to the growth of higher quality films having nanostructural properties providing opportunity for new fundamental studies that lead to various applications**(Ismail et al., 2013)**. The current growth of nanostructured CdO has led to gas-sensing applications including detection of liquid petroleum gas (LPG), CO2 and NO2**(Mei et al., 2020)**.Thus, nanostructured CdO films can be used in environmental monitoring devices to detect gases that are hazardous to the wellness of humans and other living beings**(Saha et al., 2008)**. Different methods are employed to prepare CdO thin film such as, sol-gel, thermal evaporation, sputtering, chemical bath deposition, spray pyrolysis, spin coating and vacuum

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evaporation**(Helen et al., 2016; Helen et al., 2018)**. Thin films are generally coated on materials called substrates to obtain the desired properties. The substrates provide the mechanical support without altering its characteristic features. Thin films of metals, semiconductors, insulators or dielectrics are prepared by various preparative techniques along with innovative methods to deposit materials with reproducible physical properties. The present work reports the synthesis and characterization of undoped CdOand Cu & Zn doped spray pyrolysed CdO thin films..

2. INVESTIGATION PROCEDURES

2.1 Materials

Cadmium acetate dihydrate ($Cd(CH_3COO)_2 \cdot 2H_2O$) (Sigma-Aldrich, India , 99.9%), copper oxide CuO, zinc acetate (ZnAc) (99%, Merck, India, 95%) and distilled water.

2.2 Fabrication of Thin film and their Studies

Cadmium acetate dihydrate was dissolved in distilled water at room temperature and water was used as solvent to synthesize CdO thin films using the spray pyrolysis technique. Copper oxide and Zinc acetate was the source for Cu & Zn doping and the concentration of the dopant was taken as 3 wt% of both the compound. The glass substrate is placed at the distance of 18 cm from the nozzle tip**(Helen et al., 2018)**. For all the films, 3 ml/min flow rate and 300 °C parameter is adopted for spraying on the substrate. The substrate was allowed to get heated to certain temperature before spraying. X-ray diffraction analysis was performed using X ray diffractometer (Shimadzu X-600) in order to study the crystal structure of the spray pyrolysed thin films. The surface morphology was recorded using scanning electron microscope (SEM, JEOL 2 – JSM 6000). Optical transmission spectra of all the deposited films were obtained using UV-VIS spectrophotometer (UV Vis NIR Jasco V-670). The electrical studies were carried out using Hall Effect measurement system (ECOPIA, HMS 3000).

3. RESULTS AND DISCUSSION

3.1. Structural Studies

The x-ray diffraction patterns were recorded for the undoped and Cu & Zn doped CdO thin films as shown in figure 3.1. The peaks corresponding to planes (111), (200) and (311) are seen on the diffractograms of the CdO films which display the random orientation of the crystallites having the polycrystalline nature. The highest intensity peak is due to (111) plane which records the undoped and Cu & Zn doped CdO films. The CdO: Cu & Zn X- ray diffraction patterns are well matched with JCPDS Card No: 05-0640 which represents the cubic structure. The Cu doping has higher intensity peaks and the growth orientation has (111) plane. This may be due to the higher quantity of cation incorporation of Cu dopant in the CdO thin films **(Kumaravel et al., 2012)**. The crystallite size D values were determined by using the Scherrer's formula given below

$$D = \frac{0.9\lambda}{\beta \cos\theta} \text{---------------} \quad (1)$$

⍰ cos⍰ where D is grain size, λ is the X-ray wavelength, β is the angular line width of half maximum intensity, and θ is the Bragg's angle.**(Selvakumar et al., 2019)**.

The average crystallite size is for doped films as it varies from 14 to 28 nm. Calculated micro structural parameters are listed in Table 1.Higher annealing temperature provides more energy that would cause a decrease of defects in the films and thus improve the crystalline quality.

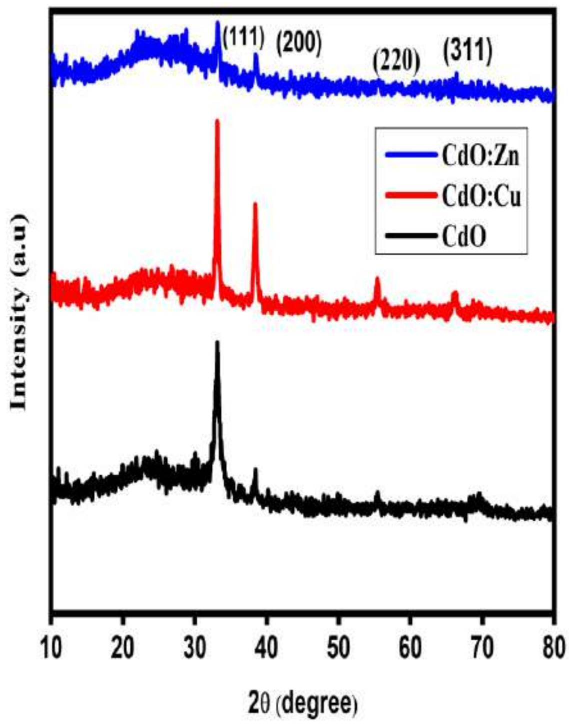

Fig-1: XRD patterns of undoped Cu & Zn doped CdO thin films (a) 0 wt. %, (b) 3 wt. % (c) 5 wt. % (d) 7 wt. % Structural parameters of undoped and doped CdO thin films.

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Table-1: Micro structural parameters (D, δ and ε) of CdO and Cu & Zn doped CdO thin films.

Samples	2θ (200) Degree	FWHM (radian)	D (Scherrer) (nm)	Microstrain ($x10^{-3}$) using formula	Dislocation density ($x10^{15}$)m^{-2}
CdO	32.95	0.59	14	405.264	405.264
Cu doped CdO	33.19	0.34	24	703.690	703.690
Zn doped CdO	33.1	0.29	28	824.824	824.824

3.2 Surface Morphology- SEM

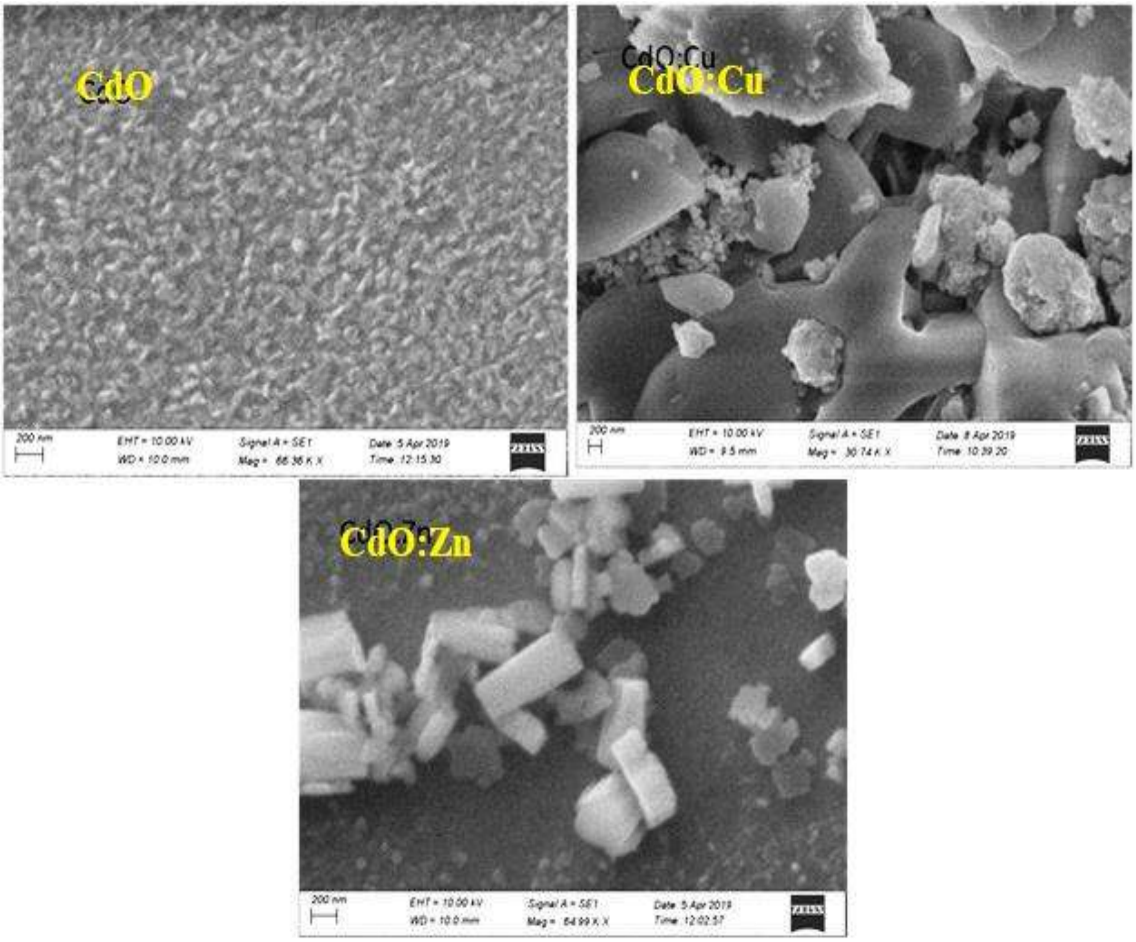

Fig-2: SEM images of undoped and Cu & Zn doped CdO thin films

The SEM images were shown in fig 3.2. Pure CdO reveals that the surface is smooth and the particles are seen in equally spread through the substrate. In Cu incorporated to CdO we can seen rough surface and particles are in bigger size**(Helen et al., 2016)**. Zn doped CdO films seen that the surface of the particles are not equally spread on the substrate.

3.3 Optical properties

Optical transmittance spectra of undoped and Cu & Zn doped CdO thin films were recorded between of 300 to 1000 nm as revealed in Fig 3.3. As the Cu & Zn doping level increases, the optical transparency (70%) increases for pure CdO thin films without doping which records the highest transparency. For Cu & Zn dopant

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the decrease in the transmittance may be accounted by the absorption of free carriers. Cu doped has transparency is very low because in the SEM images rough surface. Determination of band gap using Tauc plot is shown in Fig 3.3. The absorption coefficient (α) and incident photon energy (hν) are related by the Tauc plot using the relation

$$(\alpha h\nu) = A(h\nu - E_g)^n \text{---------------} \quad (2)$$

where hν, A and Eg are the photon energy, energy dependent constant and optical band gap respectively. The value n is a constant related to the nature of electronic transitions, for the direct allowed transitions, n has a value of ½ while for the indirect allowed transition n has a value of 2. Extrapolation of the linear portion of the curve to meet $(\alpha h\upsilon)2= 0$ determines the optical energy band gap, Eg. Fig 3.3 the pure CdO has a band gap of 2.28 eV while pure CdO. The optical band gap of Cu & Zn doped films are determined as 2.24, 2.26 eV respectively. Decrease in band gap of Cu doping film can be explained on the fact that the shifting in the Fermi-level will vary the band structure of the film resulting in the formation of new donor levels in the forbidden band gap. It occurs once the carrier concentration goes beyond the conduction band edge density of states due to the degenerate doping in semiconductors.**(Vijayaprasath et al., 2014)**. As the concentration of doping increases more than the donor states, the Fermi level is pushed to higher states of energy. The Moss –Burstein shift in the band gap value is given by equation

$$\Delta E = \hbar^2/2m^*(3\pi^2 n)^{2/3} \text{---------} \ (3)$$

Where ħ is the reduced Planck constant, m* is the effective electron mass with respect to the free electron mass and n is the free electron concentration in a single valley**(Ghosh et al., 2005)**. Thus, the blue shift in the band gap with increase in the dopant level can be related to the well known B-M energy level shift.

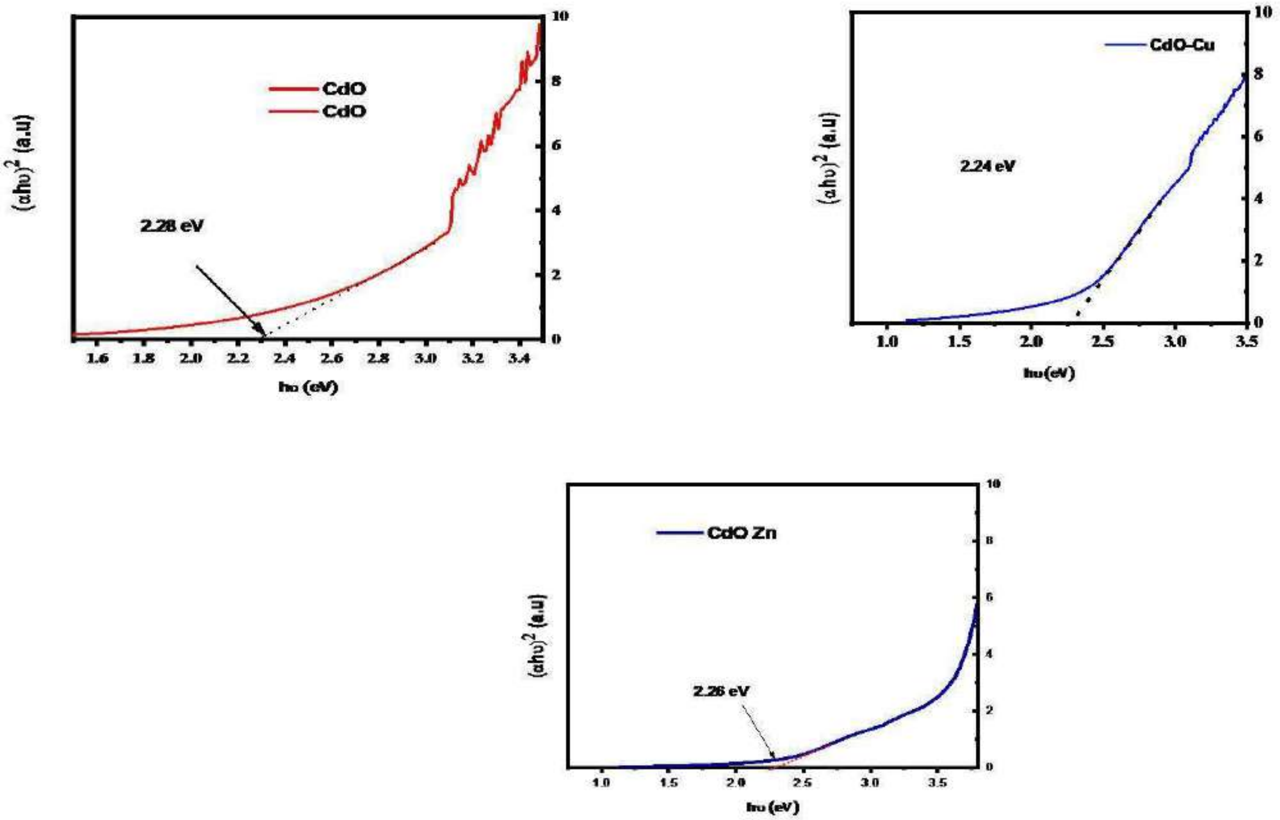

Fig-3: UV Spectra for undoped and Cu & Zn doped CdO thin films.

The electrical studies of undoped and Cu & Zn doped CdO thin films in the figure 3.4. Pure CdO has high conductivity. Cu doped CdO reveals that the films has high conductivity because of copper has naturally has high conductivity**(Santos-Cruz et al., 2005)**. Zn doped CdO has low conductivity due to high resistivity.

CONCLUSION

Pure and Cu & Zn doped CdO thin films are prepared using spray pyrolysis technique on glass substrates. The prepared were characterized by Structural, Optical and Electrical properties. XRD reveals that the films are polycrystalline nature with cubic structure. SEM images shows that the films are rough and smooth surface. Optical studies reveals that pure CdO films has high transparency and optical band gap has decreases compared to undoped CdO thin films, In the electrical studies reveals that Cu doped CdO has high conductivity.

Conflicts of Interests:

The authors have no conflict of interest to declare.

Contributions:

The first author served as the lead researcher and conducted Conceptualization, Investigation, Formal analysis, Data Curation, and Writing. The second author provided Supervision. The authors have read and approved the final manuscript.

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