Arabian Journal for Science and Engineering (2019) 44:6631–6636
https://doi.org/10.1007/s13369-019-03823-9

RESEARCH ARTICLE - PHYSICS

Crystallographic, Spectroscopic and Electrical Study of ZnO:CdO Nanocomposite-Coated Films for Photovoltaic Applications

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Received: 30 November 2018 / Accepted: 15 March 2019 / Published online: 13 April 2019

Abstract

In this paper, we report structural, optical and electrical properties of wide band gap zinc oxide: cadmium oxide-coated films prepared by cost-effective screen printing technique on glass substrates. Characterizations of the samples were carried out with X-ray diffraction (XRD), UV–Vis spectroscopic analysis. Fourier transform infrared (FTIR) spectroscopy and two probes for electrical conductivity measurement. The XRD patterns show polycrystalline nature of the films. It was observed that ZnO belongs hexagonal and CdO cubic crystal structures for $x = 0$ and 1% with a preferred orientation along (101) and (111) direction. While the mixed hexagonal and cubic phases were observed at $x = 30\%$, FTIR spectra show the vibrational bands pertaining to (ν Zn–O and ν Cd–O) stretching modes. Absorption spectroscopy exhibits the direct band gap transition, and optical band gap is decreased from 3.21 to 2.41 eV in ZnO:CdO nanocomposite. The Arrhenius plot of DC conductivity shows semiconductor nature with decreasing of activation energy.

Keywords Screen printing · XRD · UV–visible · FTIR and DC conductivity

1 Introduction

The synthesis of material in the form of coating is a fundamental step in many applications. Both the deposition mechanism and the material have to abide with several requirements [1].This beauty collection of physical properties is carried out by free-electron generation or hole carriers in a material possess a large energy band gap ($\geq$ 3.1 eV) so that it is non-absorbing or transparent to light in visible region [2]. In this direction, zinc oxide (ZnO) is a very well-known wide band gap semiconductor in the near ultraviolet of (3.37 eV) at room temperature (RT) and has several fundamental advantages over its chief competitor, GaN: its higher free excitonic binding energy (60 meV) than that of GaN (21–25 meV). ZnO has been a promising candidate for many applications in different fields and has already been reported [3]. Another option is cadmium oxide (CdO) with desirable characteristics like, large band gap, low electrical resistivity and high optical transmittance in the visible region of the solar spectrum [4]. Therefore, a proper incorporation of CdO into ZnO can reduce the band gap and makes the composition more useful in the fabrication of hetero-junctions for optoelectronic devices [5,6].

Various workers have deposited ZnO–CdO composite-coated films by various physical and chemical deposition techniques, like electro-deposition [7], molecular beam epitaxy [8],sol–gel process [9], spray pyrolysis [10] and screen printing method [11]. Among all these, screen printing method is very simple, forms films with good mechanical strength and optimal resistance and cost-effective method.

The authors prepared ZnO-based nanocrystalline thin films of different morphologies by sol–gel route using different sol concentrations and in other physical techniques, the sophisticated costly instruments and substrates are required that increase fabrication cost of the devices and takes more time for film deposition [12,13].

In this context, screen printing method has been employed at room temperature and requires less time for film deposition. This economic method is easily scalable for large-scale production of thick films over large surface area with very low material wastage and high uniformity. Hence proved to be, one of the very efficient thick film deposition technique. The present work focuses on the deposition of large

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area ZnO:CdO-coated films by screen printing method and to study the effect of the Zn/Cd ratio on the structural, optical and electrical properties of the films for optoelectronics applications.

2 Experimental Technique

First ZnO, CdO and ZnO: CdO nanoparticles were prepared by chemical co-precipitation route using zinc acetate dehydrate and cadmium acetate dehydrate as a reactant. The formation of zinc oxide by sol–gel process used zinc acetate as the initial reactant proceeds in three step viz. hydrolysis, condensation and polycondensation. After the evaporation of the water molecules, the final product chains of terminal hydroxylated zinc oxide were obtained which can be represented as HO (Zn–O–Zn)n –OH where n is the number of molecules taking part in the condensation process (polycondensation). During the polycondensation process, the reaction proceeds uniformly in all directions in the plane of the substrate and the crystallization becomes steady and uniform. The formation of zinc oxide by sol–gel process using zinc acetate as reaction precursor is elaborated by the following chemical equations. Zinc acetate dihydrate upon dissolution in double-distilled water exists in partially hydrolyzed and mostly in ionized state. The extent of hydrolysis depends upon the atmospheric relative humidity at ambient temperature which encourages the formation of basic zinc acetate. This solution on evaporation produces a mixture of zinc acetate and basic zinc acetate. This mixture on heating forms two molecules of $Zn(OH)_2$ which in condensation/ polycondensation reaction forms chain of Zn–O with terminal OH groups, the reaction is presented in Step 3 as :

1. Hydrolysis reaction takes place on dissolution of zinc
2. acetate in water

$$\underset{\text{(basic zinc acetate)}}{Zn(CH_3COO)_2 + H_2O} \Leftrightarrow Zn(OH)(CH_3COO) + \underset{\text{(ionized zinc acetate)}}{CH_3COOH + Zn^{2+} + 2CH_3COO^-}$$

On heating ionized zinc acetate form zinc hydroxide and acetic acid which evaporates off while basic zinc acetate hydrolyses to zinc hydroxide and acetate ions. These reactions are given as:

$$Zn(CH_3COO)_2 + 2H_2O \rightarrow Zn(OH)_2 + 2CH_3COOH \uparrow$$
$$Zn(OH)(CH_3COO) + OH^- \rightarrow Zn(OH)_2 + 2CH_3COO^-$$

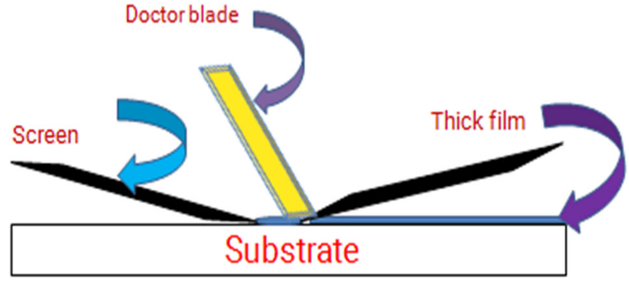

Fig. 1 Schematic screen printing coating setup

3. Condensation reaction

$$HO - Zn - OH + HO - Zn - OH \rightarrow HO - Zn - O - Zn - OH + H_2O$$

If three molecules of $Zn(OH)_2$ condense, the reaction would be expressed as:

$$HO - Zn - O - Zn - OH + HO - Zn - OH \rightarrow \underset{\text{(Polycondensation)}}{HO - Zn - O - Zn - O - Zn - OH}$$

The process would continue. After the evaporation of the water molecules, this would result in a final product which can be written as $HO(Zn - O - Zn)_nOH$ where n. is the number of molecules taking part in the condensation process (polycondensation). Since during the course of polycondensation, the reaction proceeds uniformly in all directions in the plane of the substrate, the process of crystallization becomes steady and thus uniform.

The similar reaction steps are followed in the synthesis of CdO and ZnO:CdO nanocomposite by sol–gel route. Finally, the product was dried in oven at 100°C and then crushed to fine powder by grinding process using a mortar and pastel. The obtained powders were used for the deposition of ZnO, CdO and ZnO:CdO thick films on slide glass substrates, by using a typical screen printing technique as shown in Fig. 1. These films are then followed by sintering temperature at 500 °C under furnace as described in reference [11]. XRD measurements were done by advanced Rigaku diffractometer with $Cu - K\alpha$ radiation (wavelength 1.54 Å) to investigate the crystal structure. The optical absorbance spectra and Tauc's plot were collected using a UV–Vis spectrophotometer (Hitachi-3400).The IR reflectance spectra were recorded by (SHIMAZU-8400S). DC conductivity was measured by Keithley electrometer, KT-105.

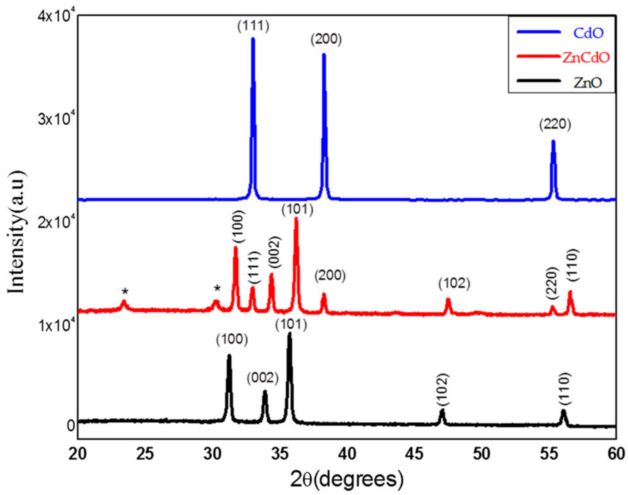

Fig. 2 XRD pattern of ZnO, CdO and ZnO:CdO-coated films

3 Results and Discussion

3.1 X-ray Diffraction Analysis

The crystalline properties and material phases of the ZnO, CdO and ZnO:CdO-coated films were studied structurally by means of XRD measurements in the scan range of 20 °–60 ° which are shown in Fig. 2. The pure ZnO film exhibited the hexagonal wurtzite which is well in consistence with standard JCPDS No: 36-1451. The observed peaks correspond to the (100), (002), (101), (102), (110) (103), (200), (112), (201), (004) and (202) planes of ZnO. While CdO-coated film has the cubic structure with diffraction peaks indexed as (111), (200) and (220) planes of CdO. It is matched well with the standard data of JCPDS No: 05-0640. For both ZnO and CdO compounds, mixed crystallite phases of with hexagonal and cubic structures were found. This is due to the larger ionic radius of Cd compared to Zn. The diffraction patterns of both ZnO and CdO were observed in case of ZnO/CdO nanocomposite, a similar report has been reported in the literature [14,15].

The follow parameters of the most oriented peak have been obtained from below formula's [16] and are listed in Table 1.

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

where λ is wavelength (Cu–K α), β is full width at half maximum (FWHM), θ is diffraction angle.

The dislocation density (δ) is calculated from D using Eq. (2).

$$\delta = \frac{1}{D^2} \quad (2)$$

The strain (ε) present in the films is calculated from Eq. (3).

$$\varepsilon = \frac{\beta\cos\theta}{4} \quad (3)$$

In the present study, it is observed that the dislocation density and strain are increased as the grain size of ZnO decreased due to substitution of bigger Cd ions (ionic radius 0.97Å) in the hexagonal wurtzite ZnO structure at smaller Zn ions (ionic radius 0.74 $Å^0$) [17].

3.2 Optical Absorption Studies

The calculation of the band gap of the synthesized coated film is the essential parameter to find the right kind of light required for solar cell application. The UV–visible absorbance spectra of CdO, ZnO and the ZnO/ CdO nanocomposite in the wavelength range 300–1200 nm are shown in Fig. 3. All the three synthesized samples show absorption in UV visible region (CdO and ZnO). The absorbance increased as the CdO concentration increased in the films, due to the increased optical scattering of incident light on the film surface [18,19]. Compared with the optical absorption of pure ZnO and CdO (387 and 513 nm), CdO/ZnO hybrid nanocomposite has absorption edge at 434 nm. The absorption edge for the CdO/ZnO hybrid nanocomposite indicates that the ZnO can be responded to the visible region by combining with CdO nanoparticles, a similar trend has been observed in the literature [20].

To determine the optical band gap, we used the Tauc's relationship:

$$\alpha h\nu = A\left(h\nu - E_g\right)^n, \quad (4)$$

where α indicates the absorption coefficient, A is taken as constant, h represents the Planck's constant, υ is the frequency of the incident photon and E_g is the optical band gap and the exponent n usually depends upon the transition type, n 1/2, 2, 3/2 and 3 denote to allow direct, indirect, forbidden direct and forbidden indirect transitions, respectively. From the analysis, we take $n = 1/2$ (direct transition characteristics)

Table 1 XRD parameters of the samples are given below

Sample	Crystal size (nm) (D)	Dislocation × (10^15 lines/m^2) (δ)	Strain × (10^-3 lines/m^4) (ε)
ZnO	28	1.27	1.30
ZnOCdO	25	1.6	2.29
CdO	21	2.26	2.55

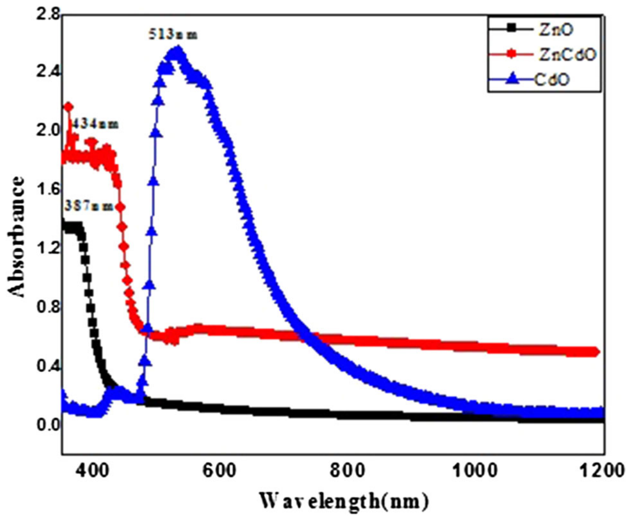

Fig. 3 Absorbance spectra of ZnO, CdO and ZnO:CdO-coated films

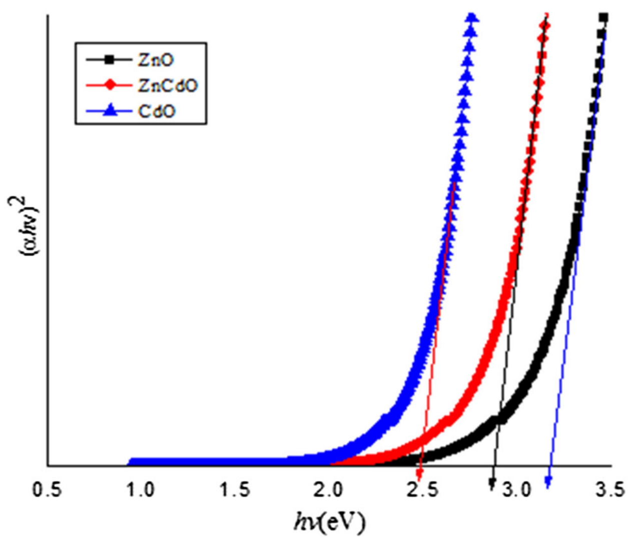

Fig. 4 Tauc's plot of ZnO, CdO and ZnO:CdO printed films

for CdO, ZnO and ZnO/CdO hybrid nanocomposite and E_g value was obtained by the extrapolation of the plot of $(\alpha h\upsilon)^2$ as function of the incident energy $h\nu$ as shown in Fig. 4. The band gap values were concluded from the linear region of the plot $(\alpha h \upsilon)^2$ vs. $h \upsilon$ curves of ZnO, CdO and CdO/ZnO hybrid nanocomposite. The obtained values of optical band gap for CdO, ZnO and ZnO/CdO hybrid nanocomposite are 3.21, 2.41 and 2.87 eV. With the doping of Cd, the optical band gap decreased. The optical absorption edge was red shifted with the doping of Cd from ZnO to CdO [21].

3.3 FTIR Spectroscopy

Infrared reflectance spectra of ZnO, CdO and ZnCdO samples were recorded in 500–4000 cm^{-1} region at ambient temperature and are shown in Fig. 5. Each spectrum is an average of 64 number of scans at 4 cm^{-1} resolution. In 1500–4000 cm^{-1} region, the vibrational peaks pertaining to atmospheric moisture adsorbed water, methyl and carbon dioxide molecules bending and stretching vibrational peaks are observed as strong, medium and weak intensity peaks. Water (H–O–H) bending and stretching modes appear at [1576, 1640 cm^{-1}] as very weak components and broad strong band at 3536 cm^{-1}, respectively. The existences of these peaks confirm the presence of adsorbed moisture from the air, and the broadness of stretching mode is attributed to the hydrogen-bonded water molecules in these samples. The broad weak peaks at 2938 and 2180 cm^{-1} arise from methyl/methylene group C–H stretching and atmospheric carbon dioxide O–C–O stretching modes, respectively. A very strong peak at 1267 cm^{-1} in both pure ZnO and ZnO/CdO nanocomposite is obtained from bending mode of Zn–O–H of zinc hydroxide which was formed during sintering process and completely decomposed to form zinc oxide. The stretching mode of Zn–O is observed as a very weak peak at 574 cm^{-1}.

In Cd–O zoomed spectrum for the region 550–950 cm^{-1}, the antisymmetric and symmetric stretching modes of Cd-O bond are clearly visible at 876, 854 cm^{-1} and 642, 674, 716 cm^{-1}, respectively [22].

3.4 Electrical Properties

The electrical characterization is very important tool for photovoltaic identification of the material. Figure 6 shows the variation of conductivity with temperature of the ZnO, CdO and ZnO:CdO-coated films and it is observed the conductivity increases with the increase in temperature. With the addition of cadmium oxide to zinc oxide, the resistivity has decreased as observed because CdO is less resistive than ZnO and thus moderates the conductivity of ZnO:CdO film and the conduction mechanism is the thermally activated type [23]. For thermally activated band conduction, the conductivity σ can be expressed as:

$$\sigma = \sigma_0 \exp\left(\frac{-\Delta E}{KT}\right) \tag{5}$$

where σ_0 is the pre-exponential factor, E is the thermal activation energy for generation process is Boltzmann's constant and T is the temperature (in Kelvin). The values of activation energies have been determined from the slope of graph and comes out : 0.37 eV, 0.33 eV and 0.30 eV for ZnO, ZnO:CdO and CdO-coated films [24,25].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.

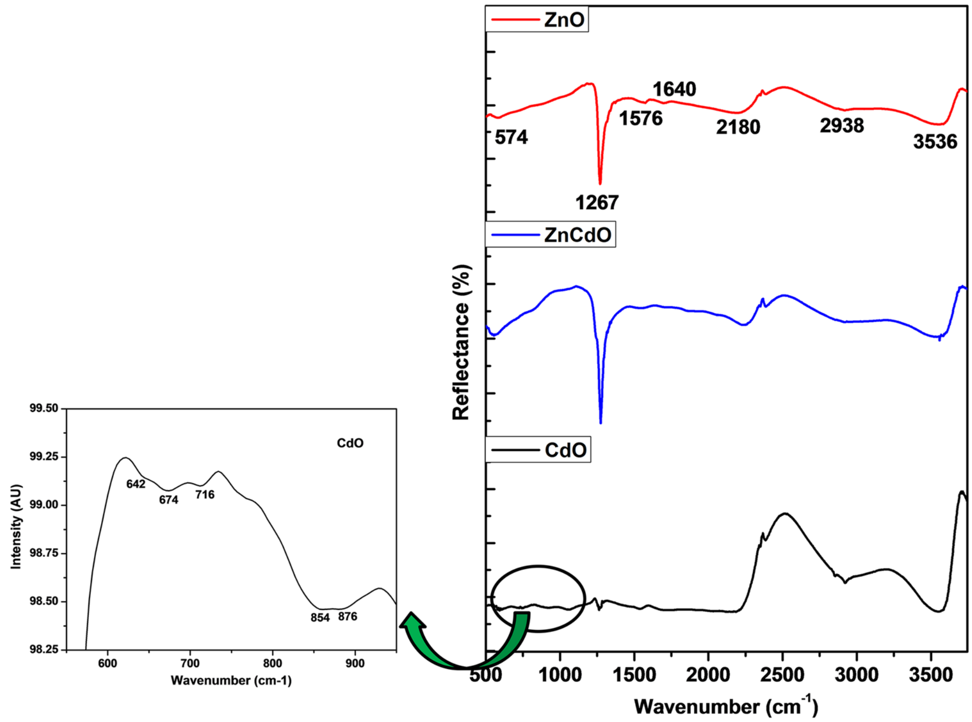

Fig. 5 FTIR spectra of ZnO, CdO and ZnO:CdO-coated films along with CdO zoomed spectrum

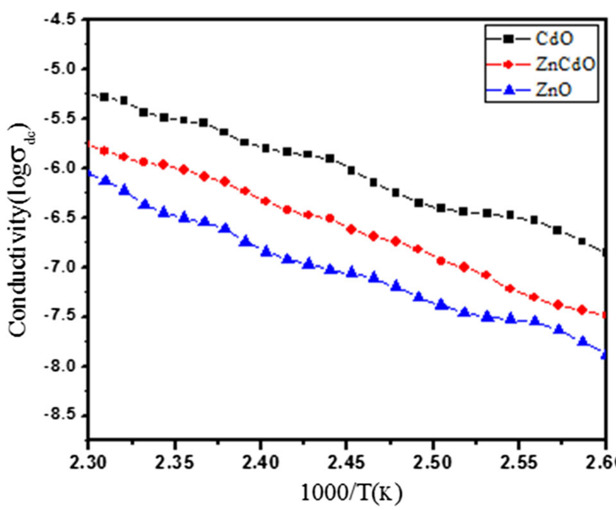

Fig. 6 Arrhenius plot for DC conductivity of ZnO, CdO and ZnO:CdO-coated films

4 Conclusion

The structural, optical and electrical properties of ZnO–CdO films prepared by a screen printing method were studied from the view of their optoelectronic application. The XRD pattern exhibits polycrystalline, mixed phases with improvement in crystallinity were found upon CdO content. From the optical analysis, it was found that the absorbance increases while band gap of the sample decreased with an increasing CdO concentration. FTIR spectrum is showing strong absorption bands between 1200 and 500 Cm^{-1}, respectively. The conductivity increases with increasing temperature. This suggests that Zn–CdO is a desired band gap material formed by suitably doping CdO into ZnO; thus, ZnCdO is an appropriate as a window material in photovoltaic applications.

Acknowledgements The author Dr. R.A. Zargar expresses sincere thanks and appreciation to the Honorable Vice-Chancellor, Professor Javed Musarrat of Baba Ghulam Shah Badshah University-Rajouri (J&K) for giving me the opportunity of R&D and teaching in the Department of Physics of this peaceful campus. Special thanks goes to Prof. Iqbal Parwez (Dean Academic Affairs) and Dr. Ashfaq Ahmed Zarri (Registrar) of BGSBU for all the moral and technical support throughout this tenure.

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