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Effect of Cu incorporation on optoelectronic properties of e-beam evaporated ZnO thin films by Ellipsometric investigations

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Abstract

Electron beam deposition technique has been used to deposit a series of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ nanocrystalline thin film on silica substrate with a variety of Cu concentrations. The microstructural, surface morphology and spectroscopic ellipsometry (SE) were used to examine the physical properties of the deposited films. The nanocrystalline nature of the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.20$) thin film has been confirmed by surface morphology studies. The XRD spectrum of the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ nanocrystalline film showed a hexagonal wurtzite type structure, and no extra phase was detected. Our results show that as the Cu content increases, the direct optical energy gap E_g decreases without any sign of solubility limit up to $x \leq 0.2$. The decrease in E_g can be attributed to the sp-d exchange coupling. In addition, exploring the spectral behavior of the refractive index dispersion from SE of the Cu-doped ZnO shows that as the Cu dopant increments; the refractive index of the deposited film enhances. Further, understand the refractive index dispersion of the deposited film has been performed using a single oscillator model proposed by Wemple-DiDomenico (WDD). Our calculations show that as the Cu concentration increases, the values of oscillator energy E_o decreases however, the dispersion energy E_d increases. As a result, the variation of the optical energy band gap and the tunability of the dispersive oscillator parameters values E_o , E_d , n_0 , ϵ_0 , M_{-1} and M_{-3} with the increase of the Cu doping level confirm that Cu doped ZnO films are a good candidate for optoelectronic device applications.

Keywords:

spintronic applications, Magnetic semiconductors oxide; Nanocrystalline, surface topography, physical properties.

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1-Introduction

Zinc oxide (ZnO) is still a promising semiconductor, because it has a high exciton binding energy of 60 meV at room temperature, direct wide band gap of 3.37 eV [1], chemically stable, good transparency in the visible wavelength, high electronic conduction, good luminescence at room-temperature, cheap, and low toxicity matter. As a result of these fascinating properties, ZnO is very suitable for use in many applications, such as optoelectronic devices [2], photocatalysis [3], solar cells [4], UV fabric protectors [5] and gas sensing devices [6]. Many workers have already fabricated ZnO films using various techniques, including spray pyrolysis [7], reactive magnetron sputtering [8,9], chemical vapor deposition (CVD) [10], sol-gel [11] molecular beam epitaxy [12], and pulsed laser deposition [13, 14]. Recently, a lot of researchers increase the potential of using ZnO by doping it with transition metals like Fe, Mn, Co, Ni and Cu [15]. Among the family of transition metals, Cu is very important metal for doping due to its high electrical conductivity and almost similar ionic radii as that of ZnO. Literature studies show that Cu doping into ZnO matrix can enhance its various physical, chemical and optical properties [16]. Commonly, doping causes the appearance of new acceptor levels and electron donors in the band structure of the doped material. These levels appear in the gap, between the conduction band and the valence band [17, 18]. The theoretical investigation shows that Cu doping can reduce band gap of ZnO leading to shift of the luminescence [19]. For copper doping, studies have shown that 5%–10% Cu-doped ZnO has a lower band gap value than undoped ZnO [20, 21]. The crystallite size of the film increased as the doping ratio of Cu increased from 2 wt % to 10 wt %. Increase in Cu doping leads to an insignificant decrease in the optical band gap of the thin films [22] and the nanoparticles were within the 32–38 nm range and the Cu dopant uniformly substituted Zn positions [23]. Other results show that Cu doping did not lead to the formation of a secondary phase, but slightly reduced the particle size [24] and the valence

state of Cu in ZnO was confirmed to be +2. It was found that the impurity level of 0.1% copper element is above the Fermi level, indicating that Cu-doped ZnO is a p-type semiconductor [25].

The manuscript is summarized as follows:

- Part 2 describes the physical method used to produce and characterize nanocrystalline $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.2$) in powder and thin film forms.
- Part 3 presents the structural and microstructural characteristics of nanostructured $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.2$) thin films grown on silica glass substrates and morphology examination of the fixed-thickness nanostructured $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.2$) thin film by Atomic Force Microscopy (AFM)..
- In Part 4, the optical properties of nanostructured $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ film with different Cu contents are comprehensively studied using the SE technique.

2. Materials and Methods

Cu doped ZnO ingots with different Cu concentrations (0, 4, 8, 12, 16, and 20 at.%) have been synthesized using mechanical milling method. Analytical grades with stoichiometric ZnO and CuO powders (with a chemical purity of 99.999%, Aldrich) were mixed together and milled in a mechanical ball mill machine at 200 rpm for 6 hours. The mixture is made into disk-shaped to avoid splashing the mixture powders during the evaporation process. The prepared pure and Cu doped ZnO ingots were used as a source for thin film deposition. The ZnO and Cu doped ZnO thin films with various Cu concentrations were deposited by electron beam evaporation technique (Edward Auto 306) at room temperature. Amorphous glass with a size of (25mm×25mm) is used as the substrate. To clean the substrate carefully, the substrate was immersed in acetone for 15 minutes, and then washed with purified water for 15 minutes, and subsequently with alcohol for 10 minutes. At

last, the substrate was ultrasonically cleaned in deionised water for 15 minutes, and then was dried in air at a temperature of 100°C. The substrates and ingots have been placed in the chamber, which was then evacuated at pressure of 5×10^{-6} Pa. The pellet ingot was preheated for 5 minutes before evaporation to remove any pollutants and degas the pellets. The distance from the substrate to the source is kept at about 20 cm. The thickness of the film was adjusted at 300 nm at a deposition rate of 2nm/sec, which was controlled by a thickness monitor device (model; FTM6). More details of the deposition methodology are explained elsewhere [26, 27, 28, 29, 30, 31, 32].

2.1 Characterization techniques

X-ray diffractometer (XRD, Cu-K α = 1.54056Å, Philips diffraction 1710) was used for crystallographic investigation. The ratio of the elemental composition of the film was checked by using energy dispersive X-ray spectroscopy (EDXS). The surface morphology of the film was performed using an atomic force microscope (AFM, model MLCT-MT-A). The vertical resolution of the AFM device is about 0.2 nm. The AFM cantilever is provided by NANO-WORLD, its cross-section is 4.5x4.6 μm^2 , the length is 160 μm , and it works at a resonant frequency of 285 kHz. Both sides of the cantilever are plated with platinum-iridium of about ~ 23 nm, and the tip is sharp with radius nearly less than 10nm. Non-contact mode is used to obtain the AFM image of the film surface. Optimized scan parameters is adjusted to supply the finest picture resolution whereas maintaining the speed and size of scan at 5 ms/pixel and 1x1 μm^2 , respectively. The optical properties of nanostructured $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.2$) film were studied using variable-angle reflection SE instrument. SE apparatus has a revolving optical compensator and is also operational with a programmed retarder. The SE spectra is measured in the angular range 60°-75° with 5° steps [33, 34, 35].

3. Results and Discussions

3.1 Elemental composition analysis

The elemental composition analysis of Cu-doped ZnO films with different Cu doping levels has been performed by EDXS measurement. Fig. 1 represents the EDXS spectra ZnO, ZnO:Cu 12 at.% and ZnO:Cu 20 at.%. The spectra of the Cu doped films confirmed the appearance of three peaks corresponding to Zn, O, and Cu. The spectra further show that the peak intensity of Cu increases with the increase of Cu doping, which indicates the stoichiometry of the film and Cu ions have been successfully incorporated into the ZnO matrix.

Fig.1. EDXS analysis of the Cu (0.04, 0.12, and 0.20) doped ZnO film.

3.2 Structural and microstructure characterizations

Fig. 2(a) shows the XRD spectra of undoped and Cu doped ZnO (ZnO:Cu) thin films deposited by electron beam evaporation method at room temperature on glass substrate with different Cu concentrations of 2, 4, 8, 12, 16 and 20 at.%. The results reveal that all films have a polycrystalline like structure with three reflection lines belonging to (100), (002) and (101) diffraction planes of the hexagonal wurtzite type structure suggested the existence of the ZnO structure; see (JCPDS No. 79-0205). In addition, the XRD pattern reveals a preferred oriented grain growth toward (002) plane due to the challenge between energy of surface and strain energy [36].

Fig. 2 (a) XRD spectra of Cu doped ZnO thin films with different Cu 0, 2, 4,8,12,16 and 20 at. %, (b) The enlargement of the main diffraction peak (002) of Cu-doped ZnO film.

It is worth noting that, the XRD spectra did not show any foreign peak related to copper phases such as copper oxide and or copper cluster, indicating a successful inclusion of Cu^{2+} ions into the ZnO lattice without change of the structure of ZnO. It was found from Fig. 2(b) that the peak position of (002) plane is shifted towards lower diffraction angles (34.48-34.42 degree) due to the Strain introduced in the film by the partial replacement of Cu^{+2} ions by Zn^{+2} in the ZnO structure of semiconductor matrix with remarkable expansion in the cell volume. Fig. 3 shows the variations of the lattice parameters (a) and (c) with increasing of Cu incorporation into ZnO host lattice which are calculated from interspacing planner distance (d) and lattice indices (hkl) of the most predominantly preferred oriented peak by using the standard equation of using the standard relation of the hexagonal system:

$$\frac{1}{d_{hkl}^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}. \text{ The results show that the lattice parameters increase}$$

with the increase of the Cu doping level which is attributed the incorporation of Cu^{2+} ions of larger ionic radius (0.72 Å) by Zn^{2+} ions of smaller ionic radius (0.74 Å), see Figs 3,4. As can be seen the obtained lattice parameters (a), (c) and lattice volume values of undoped ZnO

are consistent with the standard reported value of ZnO hexagonal structure, see JCPDS No. 79-0205. This behavior was given in literature for ZnO doped Mn [37] and ZnO doped Cu thin films [38]. In addition, the nanostructure nature of the films is examined by using Debye-Scherrer's equations from the calculations of the mean crystallite sizes, $D = \frac{k' \lambda}{\beta \cos \theta}$ and lattice microstrain, $\varepsilon = \frac{\beta}{4 \tan \theta}$ where, θ , β , k' and λ are the Bragg angle of most preferred oriented peak, radian FWHM, shape factor (≈ 0.9) and the wavelength of the $\text{CuK}\alpha$ radiation, respectively. The value of the average crystallite size of the Cu doped ZnO film is found to decrease from 16.42 nm for ZnO to 12.28 nm for Cu:20 at.%, confirming the nanostructure characteristic of the film.

Fig. 3: The change of the lattice constant $a(\text{\AA})$ and $c(\text{\AA})$ in ZnO matrix with Cu content (0.0, 0.04, 0.08, 0.12, 0.16, 0.2)

Fig. 5 displays the dependence of the microstructure parameters with Cu doping, see also Table 1. It can be seen that as the Cu doping increases, the average crystallite size decreases, while the micro strain increases. This indicates that the Cu substitution slows down the

growth of ZnO grains [39]. As shown in Figure 5, the introducing of Cu ions into the ZnO matrix will cause the grain size to decrease, which is correlated to the inhibition of the nucleation growth mechanism (bad crystallinity), leading to lattice distortion [40], thereby degradation of crystallinity. This means that there is tensile micro strain embedded in the ZnO lattice. These practical observations are in accordance with the reported results of Mn-doped SnO₂ [41], Ni-doped SnO₂ [42], Mn doped ZnO [43].

Fig. 4 The change of unit cell volume in ZnO matrix with Cu content (0.0, 0.04, 0.08, 0.12, 0.16, and 0.20).

Fig.5 The change of the crystallite size D lattice strain ϵ in ZnO matrix with various Cu contents (0, 4, 8, 12, 16, 20 at. %).

3.3 Surface morphology analysis

The microscopic description of the surface morphology of the undoped and Cu doped ZnO films has been performed using AFM investigation. Fig. 6 shows the three dimensional (3D) AFM images of ZnO, ZnO:8 at. % and ZnO:16 at. % films. The images show that the surface of the films has a highly densely spherical elongated packing grain with uniform arrangement. The observed regular distribution of the elongated spherical grains with similar directions confirms the observed preferred oriented grain growth toward (002) plane. The micrographs of the ZnO and Cu doped films were analyzed in details in order to identify the microscopic surface morphology parameters, such as the grain size, surface roughness and root mean square (RMS) surface roughness. The data extracted from the images analysis show that the grain size decreases from 24.4 nm to 18.6 nm with the increase of the Cu concentration from 0 at.% to 20 at.% into ZnO lattice matrix, see our previously reported research [44, 45]. Furthermore, it was found that the surface roughness and RMS surface roughness are decreased from 4.01 nm to 3.4 nm and from 3.8 nm to 3.2 nm, respectively

with the increase of the Cu concentration from 0 at.% to 20 at.%. The reduction in the surface roughness with the increase of Cu doping into ZnO films [38] and CuTe films [46] is reported in literature. It has to be mentioning that the grain size obtained from AFM is higher than the crystallite size calculated by XRD. This inconsistency can be ascribed to the fact that the crystallite size is a record of the size coherent scattering domain, whilst the grain size is a set of this coherently scattering domain separated by grain boundary. Besides, crystallite size reveals two distinct ranges when dislocations are located in the composition, while the difference between them is not visible in the AFM micrographs [42].

Fig. 6 3D-AFM images of (a) ZnO ($x=0$) film (b) $\text{Zn}_{0.92}\text{Cu}_{0.08}\text{O}$ and $\text{Zn}_{0.84}\text{Cu}_{0.16}\text{O}$ film.

3.4 Spectroscopic ellipsometric investigation of nanostructured $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ thin films

3.4.1. SE spectrum of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ thin film

SE technique requires a polarized light beam to interact with the thin film surface at a specific incidence angle. Therefore, SE is considered as a non-contact optical technique that characterizes the optical properties of the surface on which the polarized light beam is reflected. After reflecting from the surface of the film sample, the state of polarization of the incident polarized beam will change. SE technique is to measure the change in the intensity and polarization state of the polarized beam when reflected from the film surface. The beauty of SE technique is that it can correlate the optical properties of the reflective surface with the variation in the intensity and polarization state of the polarized beam reflected from the film surface. In SE, the experimentally measured factors are the amplitude ratio (ψ_{Exp}) and the

phase difference (Δ_{Exp}) between incident and reflected polarized light waves. Using some fitting analysis, the optical constants (n & k) of the studied film can be obtained from the experimentally ellipsometric factors ψ_{Exp} and Δ_{Exp} . The spectral change of the SE factors are directly interrelated to the coefficient of amplitude reflection via the given relationship [47, 48, 49]:

$$\rho = \frac{r_p}{r_s} = \tan \psi \exp(i\Delta) \quad (1)$$

The terms r_p and r_s shown in relation 1 are the Fresnel coefficients of light waves polarized parallel to and vertical to the plane of incidence, respectively, and Δ is difference in phase between the parallel and the vertical component of the polarized wave. Spectra of ψ_{Exp} and Δ_{Exp} of the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ film with different Cu contents measured when the incident angle is equal to 70° is depicted in Fig 7(a,b). In the 600-1100 nm spectral range, the ψ_{Exp} spectra show obvious oscillations. This oscillation occurs due to the overlapping between light waves reflected from the top surface and the light waves go during the film. The spectral oscillation observed in the ψ_{Exp} spectrum indicates that the film under investigation is transparent. Near to the energy band gap of the studied film (250-590nm), the oscillation disappears, indicating that the absorption process has begun. A theoretical optical model was proposed in order to extract the physical properties of the studied film (surface irregularities, optical parameters (n & k) and film thickness) from the ψ_{Exp} and Δ_{Exp} spectra, see Fig. 7(a, b). Regarding the physical properties, the proposed model must match the actual structure of the studied film. Using the proposed optimization simulation program of the optical model of fitting parameters that matches the actual sample structure, the n and k of the studied film can

Fig.7 (a,b). For different Cu concentration ($x = 0.0, 0.04, 0.08, 0.12, 0.16, 0.2$) ZnO film, the spectral characteristics of the SE parameters Ψ and Δ with wavelength is measured at the incident angle $\theta=70^\circ$

be obtained from the matching of the experimental and simulated SE spectra of $\psi_{Exp.}$, $\Delta_{Exp.}$, $\psi_{Cal.}$ and $\Delta_{Cal.}$, respectively. By reducing the mean square error function (MSE) calculated using Levenberg-Marquardt mathematical relation, the equivalent between the measured SE parameters $\psi_{Exp.}$, $\Delta_{Exp.}$ and the calculated SE parameters $\psi_{Cal.}$, $\Delta_{Cal.}$ can be obtained. The mathematical relation of Levenberg-Marquardt is [44, 45, 50]:

$$MSE = \frac{1}{2N - M} \sum_{i=1}^N \left(\left(\frac{\psi_i^{mod} - \psi_i^{exp}}{\sigma_{\psi,i}^{exp}} \right)^2 + \left(\frac{\Delta_i^{mod} - \Delta_i^{exp}}{\sigma_{\Delta,i}^{exp}} \right)^2 \right) \quad (2)$$

The factors given in Eq.2 is; N is the number of measurement data pairs of $\psi(\lambda)$ and $\Delta(\lambda)$ included in the fitting process, M is the fitting parameters number, and i is a running discrete index of the sum. In addition, ψ_i^{exp} , Δ_i^{exp} and ψ_i^{mod} , Δ_i^{mod} are the measured and simulated

values of the SE parameters, respectively. During the average period of the rotating polarizer and the analyzer, the SE parameter standard deviation computed from the error bar of the determined calibration parameter and the irregularity of the determined data are given by ($\sigma_{\psi,i}^{\text{exp}}$ and $\sigma_{\Delta,i}^{\text{exp}}$). Soon, we reached a good agreement between the calculated results of the proposed optical model and the measured SE parameters $\psi_{\text{Exp.}}$ and $\Delta_{\text{Exp.}}$, so that the wavelength dependence of the optical constants of the studied film can be determined. In the following paragraphs, we will give more detailed discussion of the optical model developed for SE data analysis of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ thin films [51, 52 53].

3.4.2 Optical Model

The response of the film to the externally incident polarized photon field can be fully explained by its complex dielectric relation ($\varepsilon(E)=\varepsilon_1+i\varepsilon_2$) from which the optical behavior of the thin film material can be obtained. Building an appropriate optical model and using nonlinear fitting procedure, microstructure parameters such as film surface irregularity, thickness and nonuniformity of film thickness can be extracted from $\psi_{\text{Exp.}}$ and $\Delta_{\text{Exp.}}$. The proposed optical model used to simulate the measured SE parameters $\psi_{\text{Exp.}}$ and $\Delta_{\text{Exp.}}$ of the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.20$) thin film is depicted in Fig.8. The optical model consists of three-layer structure. These layers are: silica glass substrate, thin film layer of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.1$) and surface roughness layer. The Cauchy dispersion relation is used to fully predict the optical response of the substrate. In our measurement, the optical constants of the silica substrate can be easily extracted from applying fitting procedure offered by software obtained from J. A. Woollam Company [**Error! Bookmark not defined.**]. The substrate optical parameters extracted from the ready use Woollam software are very consistent with the values reported in the Hand book of optics [54]. Thin film layer of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.20$) is modeled as a gradient index layer. In gradient index scheme the full layer thickness is separated into several sub-layers with small thicknesses inside, and the optical

characteristics of each sub-layer are marginally dissimilar from those of the nearby layers. The B-spline calculation scheme is used to really examine the spectral performance of each layers composing the actual film thickness of the nanocrystalline $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.2$) layers. Since our film is composed of three materials Sn, Cr and O, therefore, effective medium approximation (EMA) is included in the gradient index scheme to account for the existence of more than one material composing the film structure. Bruggeman EMA model is included in SE analysis through the following relation [55]:

$$\sum_{i=1}^m f_i \frac{\varepsilon_i - \varepsilon_{eff}}{\varepsilon_i + 2\varepsilon_{eff}} = 0 \quad \sum_{i=1}^m f_i = 1 \quad (3)$$

In Eq.3, $m = 3$ denotes the number of component materials that make up the film, the effective dielectric function is denoted by ε_{eff} , and also the volume fraction and complex dielectric function of component i are expressed by f_i and ε_i , respectively. Eq.3 is applied under the assumption of isotropy and the topological equivalence of each component; these limitations can be improved by using the general EMAs model [56]. In addition, for the sake of simplicity, it is supposed that the surface irregularity layer depicted in Fig. 10 varies as periodic function of the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.1$) oxide film and air. The SE parameters ($\psi_{Exp.}$ and $\Delta_{Exp.}$) demonstrated in the Figs.9-10, (black squares and blue dots) and the calculated data ($\psi_{cal.}$ and $\Delta_{cal.}$) shown as black and blue lines are presented. As clearly depicted in Figs. 9-10, nice coincident between the measured SE parameters ($\psi_{Exp.}$, $\Delta_{Exp.}$) and the calculated SE parameters ($\psi_{cal.}$, $\Delta_{cal.}$) in the entire recorded wavelength regime is achieved. The MSE values generated by the harmony between measured and calculation SE parameters are 1.12 and 1.11 for ZnO and $\text{Zn}_{0.84}\text{Co}_{0.16}\text{O}$, respectively. In addition, the fitting activity also produce approximate value for the thickness of the film and surface irregularity which are $214 \pm 0.44 \text{ nm}$, 3.90 nm , $211 \pm 0.41 \text{ nm}$ and 3.60 nm for ZnO and $\text{Zn}_{0.84}\text{Co}_{0.16}\text{O}$, respectively. As

we have noticed, the surface irregularity extracted from the SE fitting scheme is in very good coincidence with the value obtained from the AFM measurement reported earlier in the morphology investigation section.

Fig.9. An optical model constructed for describing measured SE spectrum of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ thin film settle on silica substrate.

Fig.9 the ψ and Δ spectra obtained by the SE measurements (black square and blue dots) of the ZnO sample at an incident angle of 70° . The solid line of different colors represents the calculated data (fitted) produced by the three-layer model.

Fig.10 The ψ and Δ spectra obtained by the SE measurements (black square and blue dots) of the $\text{Zn}_{0.84}\text{Cu}_{0.16}\text{O}$ sample at an incident angle of 70° . The solid line of different colors represents calculated data (fitted) produced by the three-layer model.

3.4.3. Absorption process occurs in nanocrystalline $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ thin film

This section is much concerned with the optical properties of nanocrystalline $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ films extracted from the previously developed optical model. First, the absorption occurs in the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ nanocrystalline film is considered, and, the spectral dependence of the refractive index of the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ nanocrystalline film is examined later. The complex permittivity ($\epsilon(\lambda) = \epsilon_1(\lambda) + i\epsilon_2(\lambda)$) of the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ nanocrystalline film is obtained as a direct consequence of the coincidence between measured SE factors ($\psi_{\text{Exp.}}, \Delta_{\text{Exp.}}$) and the calculated SE factors ($\psi_{\text{cal.}}, \Delta_{\text{cal.}}$). The optical factors (n & k) of the studied films are correlated to the value of $\epsilon_1(\lambda)$ and $\epsilon_2(\lambda)$ through the mathematical formula:

$$\epsilon_1(\lambda) = n^2 - k^2 \quad \& \quad \epsilon_2(\lambda) = 2nk \quad (4)$$

In the previous relationship (Eq.4), the factors n and k are expressed as refractive index (real part) and extension coefficient (imaginary part) of the complex dielectric constant $\epsilon(\lambda)$,

respectively. Using the following relationship, the real and imaginary parts of $\varepsilon(\lambda)$ are interconnected to optical factors of film being studied using the formula [57]:

$$n(\lambda) = \frac{1}{\sqrt{2}} [\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{0.5}]^{0.5} \quad \& \quad k(\lambda) = \frac{1}{\sqrt{2}} [-\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{0.5}]^{0.5} \quad (5)$$

The wavelength dependence of the absorption coefficient $\alpha(\lambda)$ occurring inside nanocrystalline $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ film is linked directly to the extension coefficient $k(\lambda)$ via the formula:

$$k(\lambda) = \frac{\alpha(\lambda)\lambda}{4\pi} \quad (6)$$

Fig.11 The extinction coefficient of Cu doped ZnO thin film versus wavelength with different Cu concentrations 0, 2, 4,8,12,16 and 20 at. %.

Fig.12. The absorption coefficient of Cu doped ZnO thin film samples with different Cu concentrations varies with photon energy extracted from SE measurements.

As shown in Figure 11, the spectral dependence of the parameter $k(\lambda)$ of nanocrystalline $Zn_{1-x}Cu_xO$ films with different Cr contents is calculated through the relationship $k(\lambda) = \alpha(\lambda)\lambda/4\pi$. The results presented in Fig.11 show that at shorter wavelength below 350 nm the value of k rises with increasing of Cu dopant. Since the energy of the propagated photons is quite close to the energy band gap of the investigated $Zn_{1-x}Cu_xO$ film, this behavior can be expected. Once we have the dispersion of the extinction coefficient $k(\lambda)$ then we can easily calculate the parameter $\alpha(E)$. Figure 12 illustrates the dependence of the absorption coefficient $\alpha(E)$ of the $Zn_{1-x}Cu_xO$ film with different Cu doping on the photon energy. Obviously, the onset of absorption processes close to and above the energy gap $E_g \approx 2.7\text{eV}-4.2\text{eV}$ is clearly observed, therefore, as expected the absorption coefficient $\alpha(E)$ rises up with the increment of the Cu level. In contrast, the absorption coefficient becomes almost flat (region of transparency) below 1.5eV up to 2.6eV. The apparent rapid decline of the absorption curve with decreasing photon energy is basically attributed to the absorption, in which electrons transition through

the energy gap to reach conduction band of the studied film. Using the well-known Tauc relationship, the optical energy gap E_g can be extracted using the following relationship [58]:

$$\alpha h\nu = \alpha_0 (h\nu - E_g)^n \quad (8)$$

In the previous equation (Eq.8), the parameter n refers to the index indicating the type of optical transition process and α_0 is constant. When $n = 1/2$ the optical transition referred to the allowed direct energy inter-band. According to Eq.8, E_g is derived by identifying the intersection of the linear portion of the extrapolation of $(\alpha h\nu)^2$ with respect to $(h\nu)$ at $(\alpha h\nu)^2 = 0$. The direct band gap of the $Zn_{1-x}Cu_xO$ ($0.0 \leq x \leq 0.2$) nanocrystalline film has been calculated based on the $(\alpha h\nu)^2$ vs. $(h\nu)$ diagram. Fig. 13 indicates that as the Cu concentration increases from 0.0 up to 0.2, the band gap of the film decreases from 3.286 eV to 2.934 eV. Note, the values of the energy gap of the investigated film are in accord with those given in literature ZnO (3.29 eV) [59]. Based on atomic configuration of the chemical components constituting the film, the dependence of the energy gap of the $Zn_{1-x}Cu_xO$ ($0.0 \leq x \leq 0.20$) nanocrystalline film can be understood. Therefore, we will start with the valence electronic configurations of the chemical components that make up the film structure. The bare ZnO film has crystal structure of wurtzite ZnO which belongs to the hexagonal system with space group P63mc, and the symmetry C46v. In the crystal structure of ZnO each zinc ion is surrounded by four oxygen ions to form $[ZnO_4]$. The configuration of the valance electrons composing $Zn_{1-x}Cu_xO$ are: $3d^{10}4s^2$, $3d^{10}4s^1$ and $2s^22p^4$ for Zn, Cu and O atoms, respectively. According to the reported results of energy gap calculation and photoelectron emission spectroscopy, the hart of the valence band (VB) of ZnO is mostly composed of a mixture of O 2s and Cu 3d atomic orbitals, while the upper VB is mainly O 2p with some mixed states of Cu 4s, respectively [60, 61]. In contrast, the bottom part of the conduction band (CB) of ZnO is built from 4s of Zn with strong contributions of Zn 3d, O 2s and O 2p states observed at higher energies [60]. As mentioned earlier, the interaction of different energy states of Zn and O

atoms results in the formation of wurtzite ZnO of hexagonal crystal structure [61]. When the Cu^{+2} atom is introduced into ZnO matrix, it will replace the cation site Zn^{+2} of the ZnO structure. Since both Zn and Cu atoms own d-electrons, therefore, the intra-atomic interaction for the intensely related d-electrons will form so called d-d interactions. The partial replacement of Zn^{+2} by Cu^{+2} leads to the existence of d-state of Cu^{+2} , which is energetically close to the Zn^{+2} d in VB of the ZnO matrix. The d-d interaction between Cu^{+2} and Zn^{+2} will result in the formation of a hybrid state close to the valence band of the ZnO crystal, which consequently will reduce the energy gap of ZnO [62]. Our results show that as the doping level of Cu in ZnO semiconductor matrix ($\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.2$)) increases from 0 % to 20 %, the energy gap reduces from 3.29 eV to 2.93 eV.

Fig.13. For nanocrystalline $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ films with different Cu contents the variation of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) is depicted.

3.4.4. Refractive Index characteristics of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ thin film

The refractive index of a thin film is one of the essential properties because it illustrates the interaction of photon waves propagating through the film with the material constitutes. Furthermore, it can also alter the properties of the propagating photon such as velocity of propagation (phase), optical pathway and its absorption. Technologically, the

material refractive index represents the basic layout parameter of most optoelectronic and polarization optical devices. Consequently, this section aims to analyze the optical characteristics of the dispersion of refractive index of nanostructured $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ film. For nearly fixed film thickness, figure 15 displays the wavelength dependence of the refractive index of nanocrystalline $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ for different percentage of Cu ($x = 0.0, 0.04, 0.08, 0.12, 0.16$ and 0.2). As clearly depicted in Fig.15, the refractive index (shown as symbols of different colours) of the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ nanocrystalline thin film enhances with increasing Cu level. The reason is that the refractive index of a substance is directly related to its polarizability through the Lorenz-Lorentz equation [63], where the polarizability of a material increases with the increase of the atomic radius of the atoms that make up the material. Therefore, replacing Cu with a larger atomic radius ($1.38\text{\AA}$) with Zn with a smaller atomic radius ($1.28\text{\AA}$) can increase the polarizability and consequently increasing the refractive index. This behavior is clearly manifested in Fig.15 in wide spectral range. This manner of n is very consistent with the reported results of Ni and Cr doped SnO_2 synthesized by spray pyrolysis deposition technique [42,64], respectively. In Fig. 15, solid lines of different colors represent the fitted lines of the experimentally extracted refractive index dispersion of Cu doped ZnO. The mathematical formula explaining the fitted line is the two terms Sellmeier dispersion relation, and its form is:

$$n(\lambda) = A + B/\lambda^2 \quad (9)$$

In Eq.9, two constants A and B are employed as fitting parameters.

Fig.15. The wavelength dependence of the refractive index of the as-deposited nanostructured Cu-doped ZnO Cu concentrations 0, 2, 4, 8, 12, 16 and 20 at. %.

3.4.5 Optical characteristic of dispersive oscillator parameters

By applying the Wemple and DiDomencio (WDD) single oscillator model, it is possible to have a deeper understanding of the spectral behavior of the refractive index and the dispersion energy parameter. The mathematical relationship describing the WDD model is [65, 66]:

$$n^2 - 1 = \frac{E_d E_o}{E_o^2 - E^2} \quad (10)$$

In relation 10, the factors n , E_d , E_o and $E = h\nu$ are index of refraction, dispersion energy, average oscillator energy and energy of the incident photon, respectively. These factors are related directly to the internal structure of the studied film, among them, E_d which is related to electronic oscillator strength and E_o is related to oscillator energy, and consequently to the average energy band gap of the investigated film. By analyzing the energy dependence of the factors $(n^2 - 1)^{-1}$ verses (E^2) for nanocrystalline $Zn_{1-x}Cu_xO$ ($0.0 \leq x \leq 0.2$) film below the edge of the band gap using WDD model. Rewriting Eq.10, the normal dispersion of the nanocrystalline $Zn_{1-x}Cu_xO$ ($0.0 \leq x \leq 0.20$) film will have the form:

$$(n^2 - 1)^{-1} = \left(\frac{E_o}{E_d} \right) - \left(\frac{1}{E_o E_d} \right) E^2 \quad (11)$$

Using straight line fitting technique to Eq.11, the calculated values of E_o and E_d factors are estimated from the graphical representation of $(n^2-1)^{-1}$ and $(hv)^2$ given in Fig. 16. Table 1 lists the WDD oscillator factors calculated for nanocrystalline $Zn_{1-x}Cu_xO$ ($0.0 \leq x \leq 0.20$).

Fig.16. graphical representation of the refractive index factor $(n^2-1)^{-1}$ against incident photon energy $(hv)^2$ for the undoped and Cu doped ZnO nanocrystalline thin films.

Obviously, the value of E_o of the nanocrystalline $Zn_{1-x}Cu_xO$ ($0.0 \leq x \leq 0.20$) film decreases as the percentage of Cu increases, which is expected because it is related directly to the average band gap of the studied film through an empirical relation of the form $E_o = (2 \pm 0.02) E_g^{opt(WDD)}$ [53]. Obviously, WDD approximate optical band gap $E_g^{opt(WDD)}$ is consistent with the values determined from Tauc's graph [67]. Besides, the physical interpretation of WDD formula reveals a strong relationship between E_d and the chemical structural changes of the deposited nanocrystalline $Zn_{1-x}Cu_xO$ ($0.0 \leq x \leq 0.20$) film (such as

lattice structure, chemical bonds, etc.) [Error! Bookmark not defined.]. Therefore, as the Cu content increases, the increase in E_d is associated to the increase in the observed lattice parameters, see Fig. 3. Additionally, Table 1 not only contains WDD oscillator parameters E_o , E_d but also the corresponding static refractive index $n_o = (1 + E_d/E_o)^{0.5}$ (n when $E \rightarrow 0$) and static dielectric constant $\epsilon_o = n_o^2$ for nanocrystalline $Zn_{1-x}Cu_xO$ ($0.0 \leq x \leq 0.2$) thin film. Finally, the optical spectra moment parameters for nanocrystalline undoped ZnO and Cu doped ZnO ($Zn_{1-x}Cu_xO$ ($0.0 \leq x \leq 0.2$)) M_{-1} and M_{-3} are calculated from the single oscillator parameters of WDD E_o and E_d using the following relations and listed in Table 1 [68]:

$$M_{-1} = \frac{E_d}{E_o} \quad M_{-3} = \frac{M_{-1}}{E_o^2} \quad (12)$$

Apparently, as Cu concentration increases, the M_{-1} and M_{-3} decrease. Consequently, the tunability of the optical energy band gap and dispersive oscillator parameters of Cu doped in the ZnO semiconductor matrix reveals the opportunity of using nanostructured Cu doped ZnO films in the optoelectronic device applications.

Table 1 For undoped ZnO and Cu-doped $Zn_{1-x}Cu_xO$ nanocrystalline films, the values of the optical band gap and single oscillator parameters are tabulated.

<i>Cu</i> <i>at.%</i>	E_g^{opt} (eV)	$E_g^{opt(WDD)}$ (eV)	E_d (eV)	E_o (eV)	n_o	ϵ_o	M_{-1}	M_{-3} (eV)⁻²
0	3.286	3.262	7.800	6.524	2.031	4.125	0.322	0.051
4	3.211	3.201	8.070	6.201	2.056	4.227	0.316	0.049
8	3.146	3.123	8.530	6.246	2.082	4.335	0.303	0.046
12	3.046	3.011	8.700	6.022	2.109	4.448	0.302	0.044
16	2.970	2.956	9.110	5.912	2.138	4.571	0.286	0.042
20	2.934	2.913	9.350	5.826	2.169	4.705	0.278	0.041

4. Conclusions

Nanocrystalline Cu-doped ZnO thin films with various Cu concentrations were prepared using e-beam deposition technique. The physical properties of the nanocrystalline Cu-doped ZnO films were studied by using different characterization methods such as XRD, EDXS, AFM and SE. The XRD spectrum of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.1$) nanocrystalline film shows the formation of a hexagonal wurtzite type structure without any additional phases. The morphology analysis shows that the grain size and the surface roughness decrease with increasing of the Cu doping level which is confirmed from XRD and SE investigations, respectively. It was found that the direct energy gap of the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($0.0 \leq x \leq 0.2$) nanocrystalline film decreases with the increase of Cu content. The direct optical energy band gap reduction of the studied film is ascribed to the sp-d exchange interaction. The refractive index dispersion shows that as the Cu doping level raises, the refractive index enhances. The variation of the optical energy band gap and the evaluated dispersive oscillator parameters values E_o , E_d , n_0 , ϵ_0 , M_{-1} and M_{-3} with the increase of the Cu doping level confirm that Cu doped ZnO films are good candidate for optoelectronic device applications.

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Figures

Figure 1

EDXS analysis of the Cu (0.04, 0.12, and 0.20) doped ZnO film.

Figure 2

(a) XRD spectra of Cu doped ZnO thin films with different Cu 0, 2, 4, 8, 12, 16 and 20 at. %, (b) The enlargement of the main diffraction peak (002) of Cu-doped ZnO film.

Figure 3

The change of the lattice constant $a(\text{\AA})$ and $c(\text{\AA})$ in ZnO matrix with Cu content (0.0, 0.04, 0.08, 0.12, 0.16, 0.2)

Figure 4

The change of unit cell volume in ZnO matrix with Cu content (0.0, 0.04, 0.08, 0.12, 0.16, and 0.20).

Figure 5

The change of the crystallite size D lattice strain ϵ in ZnO matrix with various Cu contents (0, 4, 8, 12, 16, 20 at. %).

Figure 6

3D-AFM images of (a) ZnO ($x=0$) film (b) $\text{Zn}_{0.92}\text{Cu}_{0.08}\text{O}$ and $\text{Zn}_{0.84}\text{Cu}_{0.16}\text{O}$ film.

Figure 7

(a,b). For different Cu concentration ($x = 0.0, 0.04, 0.08, 0.12, 0.16, 0.2$) ZnO film, the spectral characteristics of the SE parameters Ψ and Δ with wavelength is measured at the incident angle $\theta=70^\circ$

Figure 8

An optical model constructed for describing measured SE spectrum of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ thin film settle on silica substrate.

Figure 9

the ψ and Δ spectra obtained by the SE measurements (black square and blue dots) of the ZnO sample at an incident angle of 70° . The solid line of different colors represents the calculated data (fitted) produced by the three-layer model.

Figure 10

The ψ and Δ spectra obtained by the SE measurements (black square and blue dots) of the $\text{Zn}_{0.84}\text{Cu}_{0.16}\text{O}$ sample at an incident angle of 70° . The solid line of different colors represents calculated data (fitted) produced by the three-layer model.

Figure 11

The extinction coefficient of Cu doped ZnO thin film versus wavelength with different Cu concentrations 0, 2, 4, 8, 12, 16 and 20 at. %.

Figure 12

The absorption coefficient of Cu doped ZnO thin film samples with different Cu concentrations varies with photon energy extracted from SE measurements.

Figure 13

For nanocrystalline $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ films with different Cu contents the variation of $(\alpha hv)^2$ as a function of photon energy ($h\nu$) is depicted.

Figure 14

The wavelength dependence of the refractive index of the as-deposited nanostructured Cu-doped ZnO Cu concentrations 0, 2, 4, 8, 12, 16 and 20 at. %.

Figure 15

graphical representation of the refractive index factor $(n^2-1)^{-1}$ against incident photon energy $(h\nu)^2$ for the undoped and Cu doped ZnO nanocrystalline thin films.