Structural and optical properties of copper-doped ZnO thin films at different weight percentage

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ZnO thin films have been synthesized by chemical vapor deposition technique at substrate temperature 400˚C and doped with Cu at (1,3,5 wt.%). The morphologies of pure and doped ZnO films were investigated by SEM and the grain size was become larger by increasing the amount of Cu doped. From X-ray diffraction measurements, the maximum intensity peak was (002) for ZnO:Cu films at diffraction angle 34.4˚ and crystallized of hexagonal phase. Based on XPS Measurements on the surface of ZnO:Cu films, it has been found that the peak was shift to higher diffraction angle and full width half maximum of the films were become wider with increasing Cu doping. The band gap of ZnO film was 3.3 eV and it was decreased as an increasing of Cu dopant.

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1. Introduction

ZnO is one of II–VI compound semiconductors which was used with many applications such as "ultraviolet light-emitters, piezoelectric transducers, sensors and solar cells" [1]. ZnO has been a wide-bandgap with a direct energy gap approximately 3.3 eV and in the range between 3.0 to 4.0 eV by doping with metals such as Mg and Cd [2-4]. An increase in the improvement of characteristics of ZnO thin films, an effective method has been used which is doping. So, adding selective elements to ZnO films present an essential way to promote and control its electrical and optical properties [5,6]. Many elements have been added to ZnO films like Fe, Ni, Mn, Al, Au and Cu [7-9]. One of the most promising dopant is copper owing to its comparable size to Zn ion [10]. The chemical and physical properties of ZnO films have been considerably affected by Cu element. This motivating subject, the electronic state of Cu in ZnO films has been studied intensely [11-15]. To prepare ZnO films several techniques were used such as Spray pyrolysis [16], pulsed-laser deposition (PLD) [17], sol–gel [18], chemical bath deposition technique [19]. CVD is one of these methods has low cost, easy-to-use, and safe.

In this paper, Cu/ZnO films have been investigated for the evaluation of effect of doping at different weight percentage on the optical and structural properties.

2. Experimental

Zinc acetate powder was used to prepare both the pure ZnO and ZnO:Cu deposited by CVD method. First, the glass substrates were cleaned in ethanol for 5 min, distilled water and acetone sequentially before being placed in the deposition system. The suitable deposition temperature was found to be 400ºC when heating the deposition material. The mean of air flow rate was 0.5 L/min to produce the best samples. The deposition time of zinc oxide was (10 min.) for all films. The thickness of pure ZnO and doped with copper films was approximately 1 μm which was measured by the gravimetric method.

The samples were characterized by using scanning electron microscope (JEUM-JSM-6754 F) operating at 10 KeV and X-ray diffraction with (λ = 1.54178 Å). The chemical state and elemental composition of copper in Cu doped ZnO films was investigated by X-ray photo-electron

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spectroscopy. An electron energy analyzer, operated in constant pass energy mode under ultrahigh vacuum (11^{-10} mbar) was used for quantifying the kinetic energy of the photo-emitted electrons from the surface. The optical transmission spectra of the ZnO:Cu films were obtained in the ultraviolet /visible /near infrared regions using UV-VIS spectrometer up to 1000 nm.

3. Results and discussion

3.1. XRD

Sharp and intense peaks are illustrated in Figure 1(a,b,c) for Cu doped ZnO films from XRD patterns.

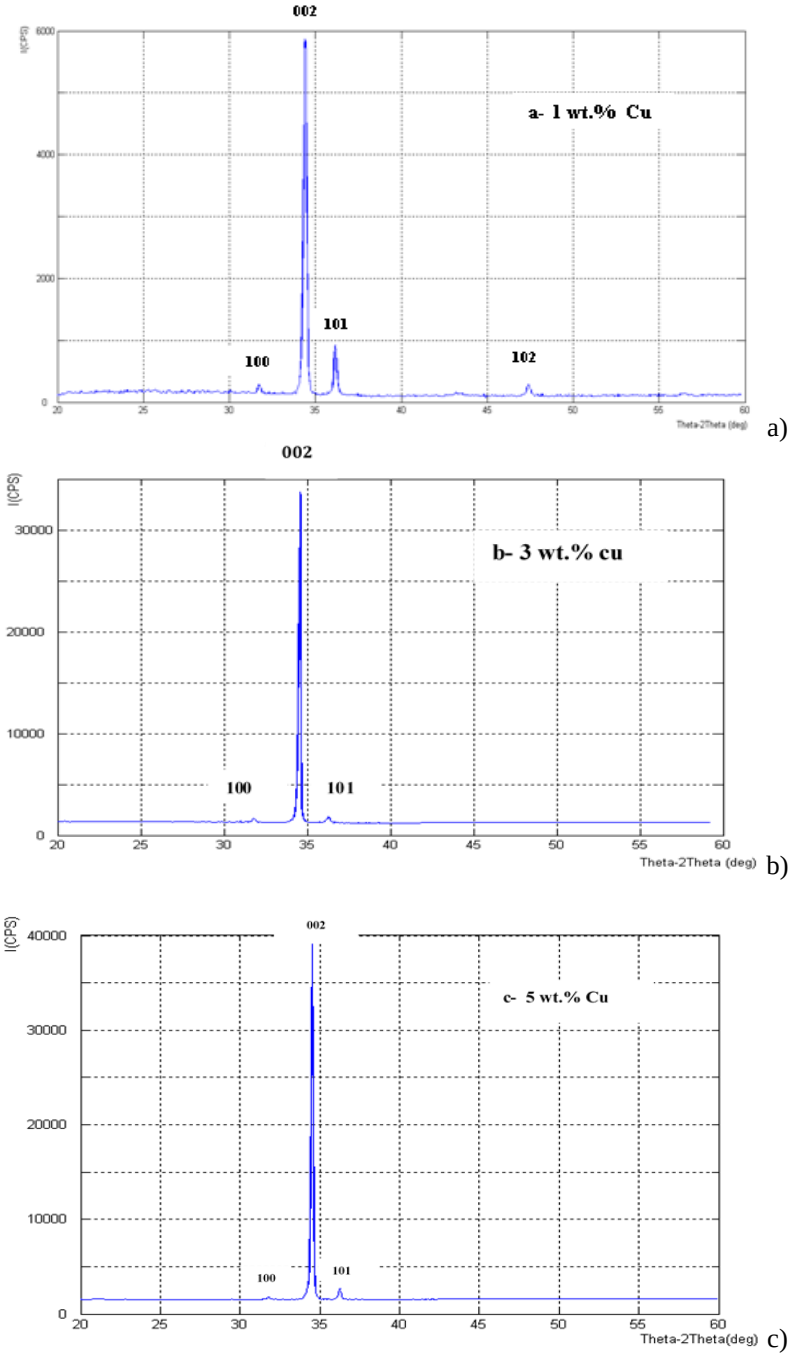

Fig. 1 XRD of ZnO:Cu films at a) 1 wt.% Cu; b) 3wt.% Cu; c) 5wt.% Cu

It was appeared at 32.2˚, 34.4˚, 36.2˚ and 47.5˚ corresponding for (100), (002), (101) and (102) planes respectively comparison of the diffraction peaks with those of the (JCPDS) No. 06-2151 and the formation of hexagonal phase for copper-ZnO doped having prominent (002) in all the films [20]. It is obvious that the intensity of peak (002) increased and the intensity of two peaks (100) and (101) are decreased with increasing the doping of Cu from (1 to 5 wt.%) and there is no copper peak of (102) plane formed after doping at 3wt. and 5wt.% because the doped copper enters the zinc oxide structure[21]. Full-width at the half maximum of the samples was become narrower with increasing at 5 wt.% Cu.

3.2. SEM

The SEM images in Figures 2 indicate that the morphology and shape for both pure and doped ZnO films at (1, 3 & 5 wt.%) Cu. Fig.2 shows the image for pure ZnO thin films with relatively non homogenous grains which have a microstructure distribution with smaller size and appearance the voids on the film surface. In the copper doped samples at (1 and 2 wt.%), the grains seem to be more agglomerated and have slightly improvement in crystallinity are shown in Fig.2(a-b). With addition of Cu dopant, the grain was become more crystalline behavior and the size and shape is larger than the other pure and Copper doped films at 5 wt.% [22] as seen as in Fig.2c.

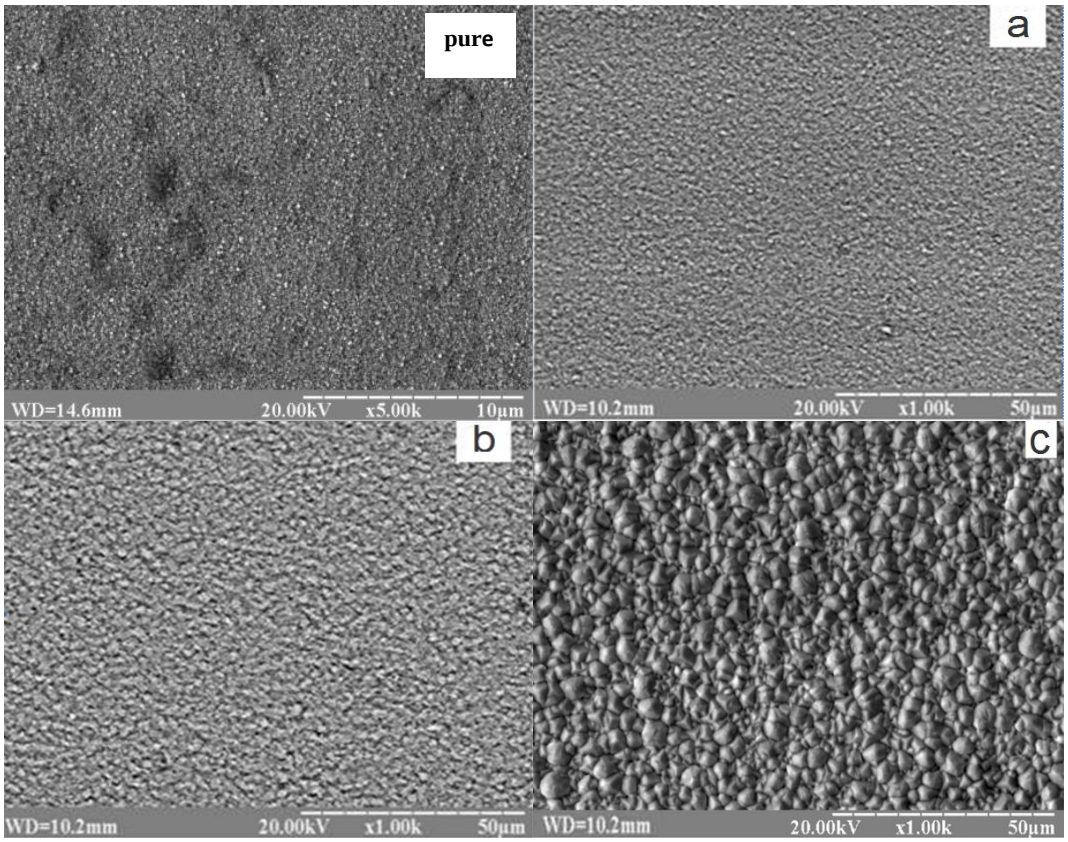

Fig. 2. SEM of ZnO films pure &doped at a) 1 wt.% Cu; b) 3 wt.% Cu; c) 5 wt.% Cu

3.3. XPS

XPS was carried out on the Cu/ ZnO films deposited at 400 ˚C at the surface as shown in Figure 3. The diffraction peaks of the ZnO:Cu films were appeared at diffraction angle 34.15˚, 34.45˚, 34.5˚ for (1, 3 & 5 wt.%) respectively as seem as in Figure 3(a,b,c). Furthermore, for higher dopant levels for these films, the diffraction peaks were broadened and shifted to higher diffraction angle which indicating a possible contraction of the ZnO unit cell [23,24]. FWHM of the samples has been become wider with increasing of Cu doped at 5wt.% Fig.3c.

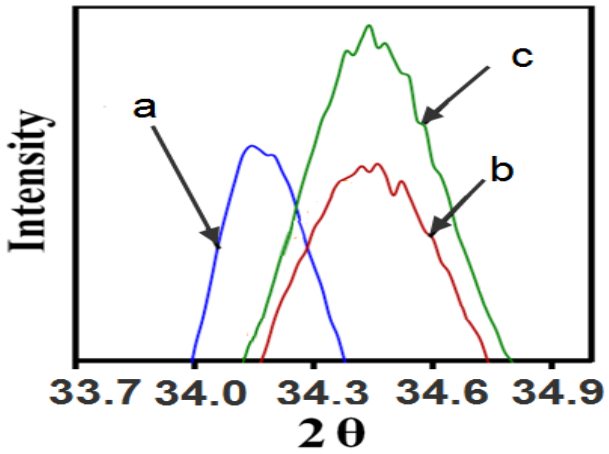

Fig.3: XPS of ZnO doped at a) 1 wt.% Cu; b) 3 wt.% Cu; c) 5 wt.% Cu

3.4. Optical properties

The measurements of the pure zinc oxide and Cu-doped films transmittance spectra were carried out in the range (320-1000 nm) at room temperature. The average values of ZnO transmittance at (0,1,3,5 wt.% Cu) in visible range were ~65%, ~26%,~%10.6 and~8.6%, respectively. It is obvious that when Cu doping increasing, the transmittance of the films is decreased as shown in Fig.4 due to the progression of Cu in the thin film that enlarges the particle size [25,26] as shown in SEM images.

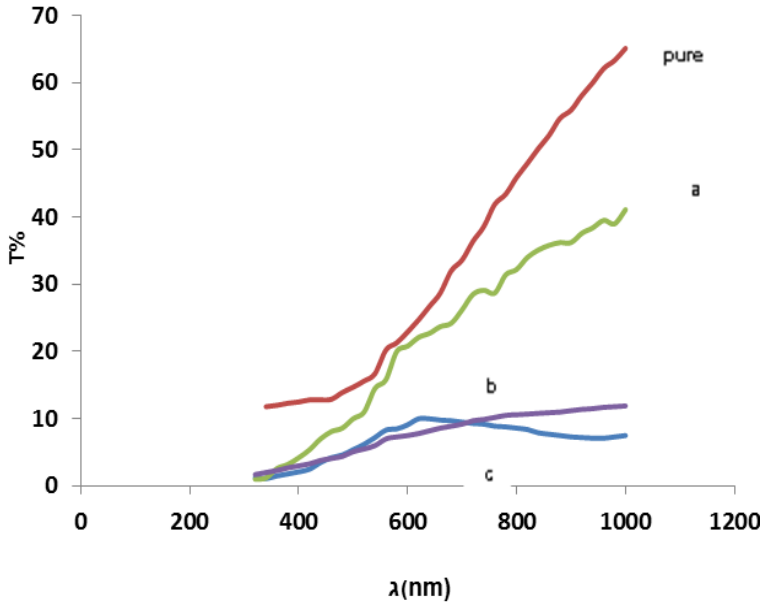

Fig. 4. Transmittance spectra of ZnO doped at a) 1 wt.% Cu; b) 3 wt.% Cu; c) 5wt.% Cu

The band gaps E_g of the films were a direct transition and were calculated for all films, by using the Tauc relationship [27].

$$\alpha h\nu = A(h\nu - Eg)^{1/2} \quad (1)$$

where α: absorption coefficient, h:Planck's constant, ν: photon frequency , for a direct band gap n is 1/2. When $(\alpha h\nu)^2 = 0$; $E_g = h\nu$ as shown in Fig.(5a-d). The increment in Cu concentration from 0

to 5 wt.% led to decrease in the band gap from 3.3 eV to 2.98 eV respectively and this results agree with [28,29]. The narrowing of the band gap due to increment in the absorbance and the impurity levels have been improved absorption in the visible range also the transition between valence and conduction bands with increase of doping [27, 28]. The increasing in the copper doping may be associated with a reduction in the density which leads to decrease the energy band gap [30,31]. Also the increase in Cu doping ratio from 0 wt. % to 5 wt. % leads to decrease in the band gap of ZnO films because the crystallite size increased as the doping of Cu increased [32].

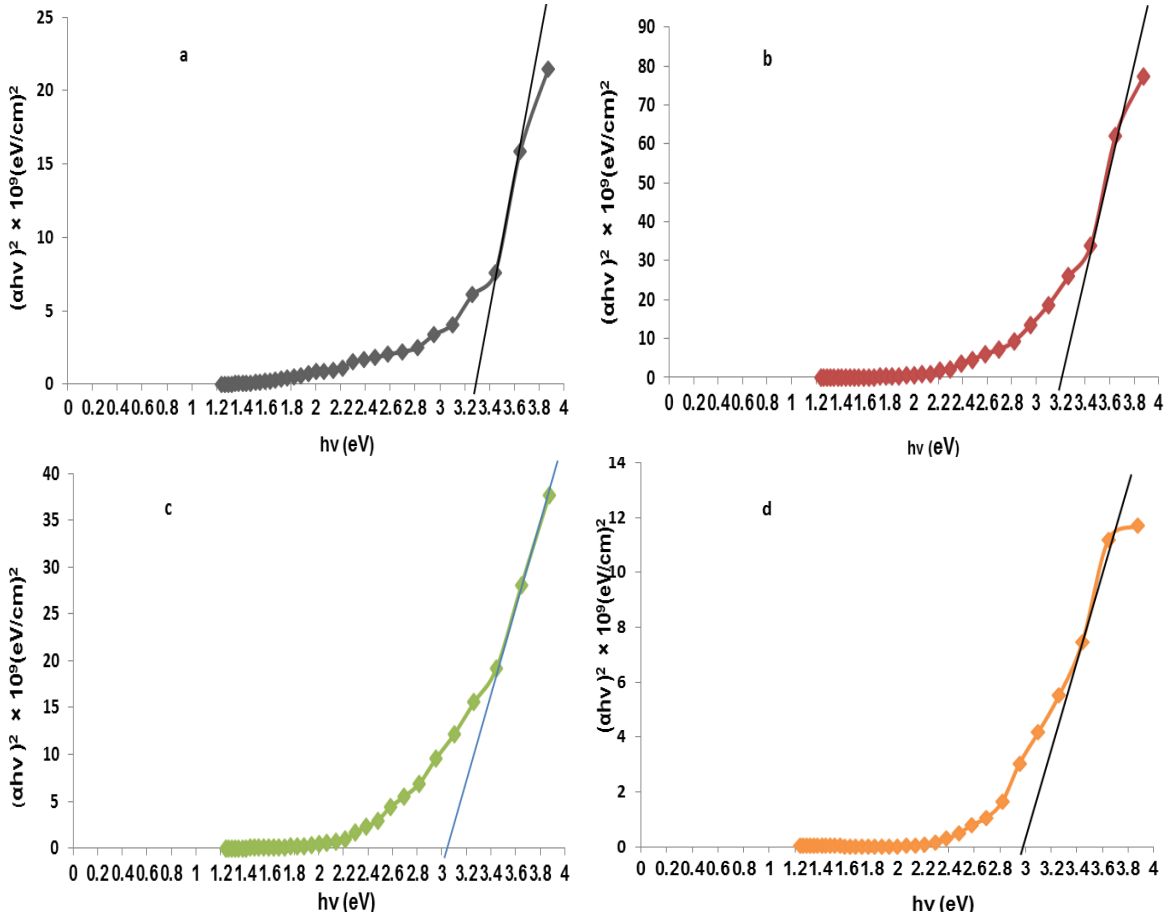

Fig. 5 Plot of $(\alpha h\nu)^2$ vs. hv of ZnO a) pure (b) 1 wt.% Cu; c) 3 wt.% Cu; d) 5 wt.% Cu

4. Conclusion

Zinc oxide films with Cu doped were deposited using CVD technique at 400 ºC. The effect of Cu dopant on the ZnO films properties are studied using XRD,SEM,XPS and UV spectrophotometer. The microstructural of the films were showed that ZnO films had been polycrystalline hexagonal structure with orientation [002]. The grains size increased with the increasing of Cu content from SEM images. The presence of Cu was also confirmed by X-ray photoelectron spectroscopy. From transmittance spectra, a direct band gap was found and it was decreased as the Cu doped in the thin films increased.

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