



# Investigation on the structural and optical properties of Zn<sub>1-x</sub>Cu<sub>x</sub>O (x=0, 0.05, 0.1) sintered films for optoelectronic device applications

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The pure and copper doped zinc oxide Zn<sub>1-x</sub>Cu<sub>x</sub>O (x=0,0.05,0.1) thick films were deposited on glass substrates by screen printing method from their nano powders, followed by sintering at 500 °C to obtain desired stoichiometry and better adherence of films. The structural and optical properties of the samples were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) with UV–visible spectroscopy and Raman spectroscopy. XRD patterns confirmed hexagonal wurtzite structure with minor detection of Cu and SEM micrographs revealed granular grains and porosity in films. The optical properties and the energy band gap of pure and Cu<sup>2+</sup> ions doped ZnO films were studied by UV–visible absorbance spectroscopy. As the doping concentration is increased, both the absorption edge and the reflectance edge is found to shift towards higher wavelengths (red shift) and the direct band gap decreased from 3.4 to 3.3 eV. The incorporation of copper in ZnO lattice is confirmed by Raman spectrum. The E<sub>2</sub> (high) phonon and multiphoton modes are observed at 441 and 1132 cm<sup>-1</sup> respectively in Raman spectra.

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## Introduction

Semiconductor ZnO has attracted extensive experimental and theoretical research efforts for its versatile applications and peculiar properties in transparent electronics, chemical sensors, ultraviolet (UV) light emitters, piezoelectric devices and spintronics since past two decades. Zinc oxide (ZnO) is one of the extensively used material in the field of optoelectronics device applications due to its wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV as compared to other semiconducting materials, viz., ZnSe (22 meV) and GaN (25 meV). ZnO possess high electrical conductivity, non-toxic nature, high mechanical stability, low cost and higher optical gain (320 cm<sup>-1</sup>) at ambient temperature which may be controlled by selecting either the non-stoichiometry and by adding suitable dopants.

Doping by other elements (e.g., Al, Ni, Mn, Pd, Cu, Fe, Cd, Ag, Au, etc.) is an adept way to coordinate the band gap of ZnO. It is known that group Ib metals (Cu, Ag, Au) are fast diffusers in compound semiconductors.<sup>1,2</sup> Among these, Cu is the best choice because the size mismatch between Cu and Zn is the smallest which leads to the lowest formation energy. In addition, electrons can be easily injected from Cu layer to ZnO since there is no barrier to the flow of electrons between Cu and ZnO.<sup>3</sup> The diffusion of Cu into ZnO can cause the formation of various centers (Cu<sub>Zn</sub>, Cu<sub>i</sub>). It is

possible that Cu atoms can replace either substitutional or interstitial Zn atoms in the ZnO lattice creating structural deformations.<sup>4,5</sup> Cu significantly affects the electrical, chemical, structural and optical properties of ZnO, and the study of the electronic state of Cu in ZnO has been the subject of interest for a long time.<sup>6-9</sup>

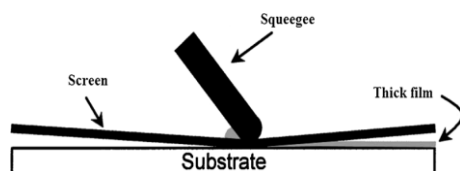
Various techniques for the preparation of ZnO films have been used such as electrochemical deposition,<sup>10</sup> cathodic electrodeposition,<sup>11</sup> radio-frequency sputtering method,<sup>12</sup> pulsed laser deposition,<sup>13,14</sup> RF magnetron sputtering,<sup>15</sup> metal organic chemical vapor deposition method,<sup>16</sup> atomic layer deposition,<sup>17</sup> ultrasonic spray pyrolysis,<sup>18</sup> filtered vacuum(cathodic) arc deposition,<sup>19</sup> screen printing,<sup>20</sup> etc. In this work, we have employed fast emerging screen printing technique to deposit ZnCuO thick films. Screen printing technique has been used as a multifaceted method for the fabrication of semiconductor layers in photovoltaic devices, especially II–IV compound semiconductors.<sup>21,22</sup> Compared to the other expensive methods, screen printing is very easier, quicker, eco-friendly and provides a reliable method for film preparation on large area substrates with maximum utilization.

Present work deals with the optimization of synthesis process and parameters for Cu<sup>2+</sup> ions doped ZnO thick films derived by screen printing technique and characterizing the variation in their structural and optical properties with increase in copper ions concentration in ZnO. The present work aims to deposit ZnCuO thick films by screen printing technique and investigate their structural and optical properties to use them in optoelectronic device applications.

## Experimental setup and measurements

Thick film paste was prepared by mixing thoroughly of pure ZnO and CuO (99.999 %) powders with anhydrous ZnCl<sub>2</sub> adhesive agent, and ground in a mortar with ethylene

glycol as a binder. The prepared paste was screen-printed on pre-cleaned glass substrates. The pre-cleaning process involves the washing of glass plates with acetone and deionized water, followed by drying at 60 °C for 10 min. The screen-printed films were dried at 110 °C for 2 hours for partial reduction of solvent and inducing porosity in the film<sup>23</sup>. The films were further annealed in a muffle furnace in an open atmosphere at 550 °C for 10 minutes so as to stabilize the films and burn the organic materials. The schematic of screen printing process used for deposition of the thick film is presented as per<sup>24</sup> and is shown in Figure 1.



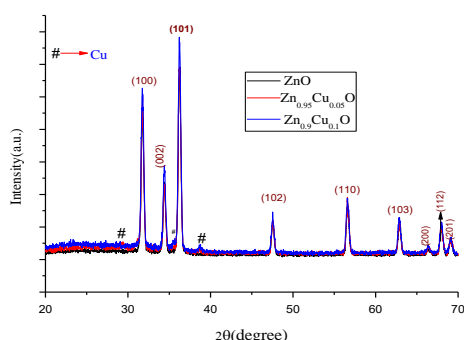
**Figure 1.** Screen-printed diagram

X-ray diffraction pattern was recorded on advanced Rigaku diffractometer in the  $2\theta$  range of 20–70° using  $\text{Cu-K}\alpha$  X-ray radiation source. The surface morphological information was derived by using scanning electron microscope (SEM, LEO-440, UK). Taylor Hobson (Taly step the UK) instrument was used for film thickness measurement that is of the order of 4  $\mu\text{m}$ . The Raman spectrum was recorded using a Horiba Jobin–Yvon laser Spectrometer 6400. The optical absorption spectrum was recorded by Hitachi Spectrometer-3900 in 200–1000 nm

## Results and Discussions

### XRD analysis

The typical XRD diffraction peaks of pure ZnO and  $\text{Cu}^{2+}$  ions doped ZnO ( $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ) powders with ( $x = 0, 0.05$  and  $0.10$ ) are shown in Figure 2.



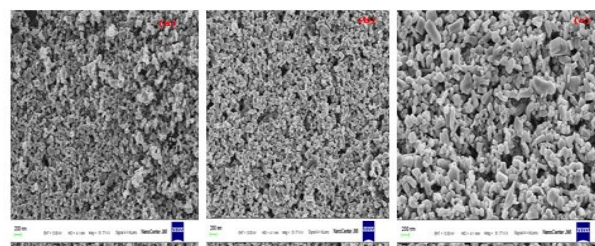
**Figure 2.** XRD analysis of ZnO,  $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$  and  $\text{Zn}_{0.9}\text{Cu}_{0.1}\text{O}$

The pronounced diffraction peaks in XRD pattern indicates the polycrystalline nature with peaks corresponding to (100), (002), (101), (102) and (110) planes as per JCPDS data card No. 65-3411<sup>25</sup>. Besides, minor Cu detection is observed at 28°, 35° and 38°. The standard diffraction peaks confirm the hexagonal wurtzite structure with space group  $P6_3mc$  of  $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ , with preferred orientation along (101) plane in all the samples, which is the most stable phase of ZnO. XRD patterns of  $\text{Cu}^{2+}$  doped ZnO

revealed that the decrease in peaks intensities with the increase in the  $\text{Cu}^{2+}$  concentration suggests the successful substitution of  $\text{Cu}^{2+}$  ions at Zn lattice site rather than interstitial one. This is due to the fact that ionic radius of  $\text{Cu}^{2+}$  (0.73 Å) is very close to that of  $\text{Zn}^{2+}$  (0.74 Å), due to which Cu can easily penetrate into ZnO crystal lattice. The particle size has been calculated from Debye–Scherrer's formula that varies from 26 nm to 29 nm, this is due to agglomeration of particles.<sup>26</sup>

### SEM analysis

Scanning electron microscopy is a convenient method for studying the microstructure of thick films. Figure 3 shows SEM micrographs of as deposited pure and copper doped ZnO thick films sintered at 500 °C.



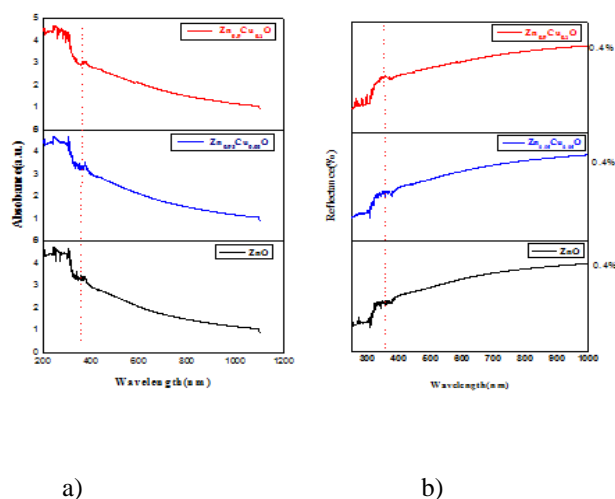
**Figure 3.** SEM analysis of Cu doped ZnO films; 3(a) pure ZnO. 3(b)  $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ . 3(c)  $\text{Zn}_{0.9}\text{Cu}_{0.1}\text{O}$

The polycrystalline structure is revealed from the SEM micrographs. The films are porous as evident from the absence of close packed morphology and interconnected grains morphology. The formation of submicrometer crystallites of varying sizes indicates agglomeration in the form of a spindle, cuboidal shaped particles with fused clusters on surface morphology in pure as well as  $\text{Cu}^{2+}$  ions doped ZnO thick films.

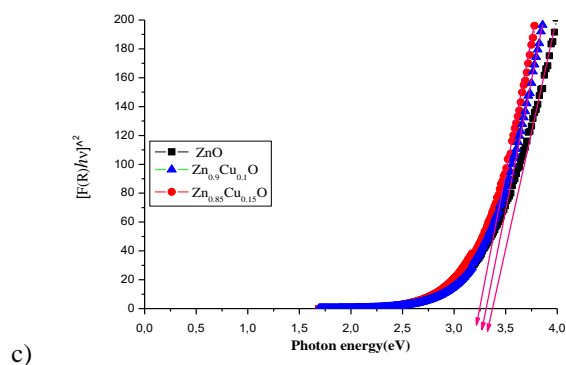
The agglomeration of small crystallites in some regions of the films makes it difficult to find the exact grain size from SEM images. The difference in surface morphology has been observed for Cu:ZnO films as compared to pure ZnO. The morphology seems to become a bit rough for Cu:ZnO thick films. It has been observed that increase in copper ion doping concentration in ZnO leads to an increase in the crystallite size which improves with the increase in mobility of atoms at the surface of films. These results also support XRD data. Hence, such types of thick films provide a novel platform for electronic device application.

### UV-Visible analysis

The optical properties and the energy band gap of pure and  $\text{Cu}^{2+}$  ions doped ZnO films were studied by UV–visible absorbance spectroscopy in the wavelength range 200–1200 nm and reflectance spectroscopy in the wavelength range 200–1000 nm as shown in Figure 4a and Figure 4b respectively. As the doping concentration increases, both the absorption edge and the reflectance edge is found to shift towards higher wavelengths (red shift). These peaks arise from the excitation of electron valence band to conduction band and are used to determine the nature and value of optical band gap.



**Figure 4.** Absorption (a) and reflectance (b) spectra of ZnO, Zn<sub>0.95</sub>Cu<sub>0.05</sub>O and Zn<sub>0.9</sub>Cu<sub>0.1</sub>O



**Figure 5.** Estimation of optical band gap using plot of  $[F(R)/h\nu]^2$  versus photon energy of ZnO, Zn<sub>0.95</sub>Cu<sub>0.05</sub>O and Zn<sub>0.9</sub>Cu<sub>0.1</sub>O

The optical band gap of the film is obtained by extrapolation of the linear portion of the graph of the modified Kubelka-Munk function  $[F(R)/h\nu]^2$  versus photon energy ( $h\nu$ ), given by the following relation.<sup>27</sup>

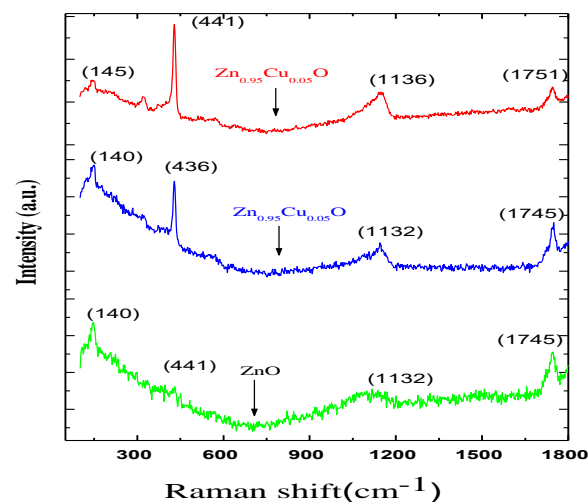
$$F(R) = \frac{(1-R)^2}{2R} \quad (3)$$

where  $R$  is the magnitude of the reflectance as the function of energy. The direct band gap comes out to be 3.40 to 3.30 eV according to<sup>28</sup> and is shown in Figure 5. This equation is usually applicable for the materials which have high light scattering and absorbing particles in their matrix. Therefore, the reflectance is effective for determining the band gap of the solar cell absorbers.

### Raman spectroscopy

Raman spectroscopy technique has been extensively used for characterizing phonon spectra of nanoscale and bulk semiconducting materials. ZnO has wurtzite structure with  $C_{6v}^4$  space group with two molecules per unit cell where all atoms have  $C_{3v}$  site symmetry.<sup>29–32</sup> Group theory predicts,  $A_1 + 2E_2 + E_1$  is the Raman active phonon modes where  $A_1$  and  $E_1$  are polar phonon modes<sup>31</sup> and  $E_2$  is nonpolar phonon

mode with two frequencies  $E_2$  (low) is associated with Zn sub-lattice vibrations and  $E_2$  (high) has been related to oxygen bonded vibrations.



**Figure 5.** Raman analysis of ZnO, Zn<sub>0.95</sub>Cu<sub>0.05</sub>O and Zn<sub>0.9</sub>Cu<sub>0.1</sub>O

Raman spectra of pure ZnO and copper doped ZnO analogs recorded in 200–1800  $\text{cm}^{-1}$  region at ambient temperature are presented in Figure 5. The Raman spectrum shows a strong, sharp peak at 441  $\text{cm}^{-1}$ . It is the significant character of the ZnO with hexagonal wurtzite structure. It corresponds to the vibration mode  $E_{2H}$  associated with the vibration of oxygen atom known as Raman-active optical phonon mode which is the strongest mode in the system of wurtzite structure.<sup>33</sup> Moreover, the appearance of a sharp peak at 441  $\text{cm}^{-1}$  reflects the presence of induced stress in ZnO wurtzite crystal structure.<sup>34</sup>

Figure 5 also exhibits the strong and asymmetric peaks at 1745 [ $2A_1(\text{LO})$ ], and 1132 [ $3A_1(\text{LO})$ ]  $\text{cm}^{-1}$  phonon modes due to the confinement of optical phonons<sup>35,36</sup> in nano-sized samples.

The weak peak at 140  $\text{cm}^{-1}$  has been observed in all the three spectra due to the induced defects. The appearance of higher order and activation of different bands is due to induced electric charge at grain boundaries with the decrease in intensity by increasing copper doping in ZnO lattice.

### Conclusion

In conclusion, the pure and copper doped zinc oxide Zn<sub>1-x</sub>Cu<sub>x</sub>O ( $x=0,0.05,0.1$ ) thick films were synthesized by screen printing technique. The incorporation of the  $\text{Cu}^{2+}$  ion into ZnO lattice rather than the interstitial was observed from XRD analysis. SEM micrograph showed porosity and agglomeration of particles occurred. From UV-visible absorbance spectroscopy it was observed that as the doping concentration was increased, both the absorption edge and the reflectance edge was found to shift towards higher wavelengths (red shift) and the direct band gap decreased from 3.4 to 3.3 eV. Raman analysis confirmed the incorporation of copper in ZnO lattice along with the observation of high and multiphonon modes.

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