

EFFECT OF CONCENTRATION ON MORPHOLOGICAL, OPTICAL AND ELECTRICAL CHARACTERIZATION OF COPPER DOPED ZINC OXIDE THIN FILMS DEPOSITED BY ELECTROSTATIC SPRAY PYROLYSIS (ESP) METHOD

ABSTRACT

Pure zinc oxide (ZnO) and copper (Cu) doped ZnO thin films were synthesized from the precursor's concentrations (zinc acetate and copper acetate) onto glass substrate via spray pyrolysis deposition technique at 350°C in air ambient, with different thickness. The films were analysed with regards to its morphological, optical and electrical properties before and after annealing. The SEM micrographs revealed that all the films were found well covered on the glass substrate. Nanofibers were observed around the nucleation centre in the pure ZnO thin films. The absorbance was recorded in the wavelength range of 230nm to 1100nm, and the optical transmission of the films was found to increase for increasing doping concentrations of Cu up to 370nm and then decreased for higher wavelength. The spectra show high transmittance (75% - 95%) in the visible and infrared regions but minimum in the ultraviolet region. The highest electrical resistivity was found to be 8.83μΩm and the lowest conductivity of 0.113MΩm⁻¹ in the films with 20%, and the refractive index of the film significantly changes with the deposition parameter and increases with increasing doping concentrations.

Keywords: ZnO:Cu, Spray pyrolysis, Electrical properties, Optical properties, Thin film

1. INTRODUCTION

Nano-composited materials are generally known for their better structural, optical, and electrical properties performances than the bulk materials in several applications such as electronics, biomedical, solar cells, catalysis, and so on. Zinc oxide (ZnO) thin films is one of the most studied group II-VI semiconducting materials that have gained interest and attention of many researchers globally due to its unique properties such as wide direct optical band of about 3.37eV and larger exciton binding energy (~60MeV) at room temperature, high transmission coefficient (>80%) in the visible and near infrared spectra, high electrical conductivity, good piezo- and photoelectric properties, thermally and electrochemically stability, and its applications in several novel devices (Hu et al., 2010; Rusu et al., 2011; Tewari and Bhattacharjee, 2011; Kim et al., 2011; Liu et al., 2005). Cu doped ZnO material has been an active research area recently, as a result of its room temperature ferromagnetism, deep acceptor level, enhanced green luminescence and gas sensitivity (Hsu et al., 2014; Rodnyi and Khodyuk, 2014). The high ionization energy and low formation energy of Cu makes it a fast diffusing impurity into ZnO lattice. Cu exhibit both +1 and +2 oxidation states depending on its chemical environment; the role of Cu in ZnO is different from other dopants such as Mn, Co, Bi, Al, Ga, B, In, Y, F, Si, Ge, Ti, Zr, Mg, and As (Behera et al., 2011). The radii of Cu⁺ (98pm) and Cu²⁺

(80pm) ions are similar to that of Zn^{2+} ion (83pm) (Rahmani et al., 2009; Behera et al., 2011). Moreover, copper is known as a prominent luminescent activator which enhances the green luminescent band by creating localized states in the band gap of ZnO (Buchholz et al., 2005; Chakraborti et al., 2007). However, the luminescent and structural properties of Cu doped ZnO nanostructures are affected by different parameters such as growth mechanisms, preheating and post annealing temperatures. The diffusion of Cu into ZnO can cause the formation of complex centres and it is possible that Cu atoms can replace Zn atoms either substitutional or interstitial (Cu) in the ZnO lattice creating structural deformations, thereby affecting the electrical, chemical, structural, morphological and optical properties of ZnO significantly (Behera et al., 2011). Several studies have been carried out in the recent years on the properties of Cu doped ZnO thin films with various deposition techniques such as magnetron sputtering, sol-gel coating, spray pyrolysis, pulsed laser deposition (PLD), chemical vapour deposition (CVD), ion plating, atomic layer deposition (ALD), molecular beam epitaxy (MBE), thermal evaporation for HTS deposition, electron beam evaporation (Islam and Podder, 2009; Sahay et al., 2007; Tan et al., 2008; Rahmani et al., 2009; Ueda et al., 2001; Chen et al., 2014; Thakur et al., 2014; Horzum et al., 2016). Among the above mentioned methods, spray pyrolysis has the advantages of being convenient, simple, low cost technique for the deposition of large area coatings without high vacuum ambience. The spray pyrolysis is a method that is well suited to control the texture through the tuning deposition parameters such as temperature, rate, thickness, continuous operation, easy fabrication and capability for uniform large area coatings. Therefore, a precise study of these properties and their dependence on the film characteristics is very essential as it helps in optimizing film parameters for designing of various optoelectronic devices based on Cu doped ZnO nanostructures. In this work, the morphological, optical and electrical properties of pure ZnO and Cu doped ZnO thin films have being studies by preparing the thin films using electrostatics spray pyrolysis technique with different thickness.

2. EXPERIMENTAL DETAILS

2.1 Reagents and Materials

Reagent grade zinc acetate, copper acetate and methanol were purchased from Merck. Ethanol, sodium lauryl sulfate, and soda lime glass substrates were obtained from Sigma Aldrich. Distilled water of pH 5.5 - 6.5 was used throughout the experiments. All reagents and solvents used for this study were of analytical grade and do not require any further purification.

2.2 Sample Preparation and Deposition

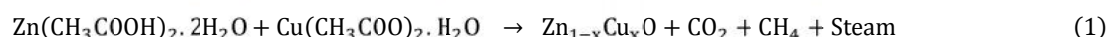
Cu doped ZnO thin films was deposited on soda lime glass substrates with home-made electrostatic spray pyrolysis system at Namiroch Material Science Laboratory, Abuja, Nigeria. The glass substrates was initially clean and degrease with sodium lauryl, rinsed with distilled water and ethanol, allowed to dry in ambient air for 10min and was then placed on the substrate heater using the substrate holder. 0.2M of zinc acetate solution was prepared by dissolving 4.39g of zinc acetate in 100ml of methanol solution and stirred for 15min in a sealed glass in order to obtain uniform solution. 0.2M of copper acetate solution was prepared by mixing 3.62g copper acetate in 100ml of methanol and stirred for

20min to obtain a homogeneous solution. To enhance the solubility of zinc acetate, 0.4ml of acetic acid was added to the solution and the concentration of the solution was kept at 0.2M. Five samples were prepared to achieve doping, the precursors were mixed by appropriate volume ratios for doping concentration as coded in Table 1.

Table 1. Sample code, Zn acetate and Cu acetate solutions at different doping concentrations of 0, 5, 10, 15, and 20%.

Sample code	Zinc acetate solution (ml)	Copper acetate solution (ml)
CuZnO ₀	10.0	0.0
CuZnO ₅	9.5	0.5
CuZnO ₁₀	9.0	1.0
CuZnO ₁₅	8.5	1.5
CuZnO ₂₀	8.0	2.0

The solutions was then moved into a commercial ultrasonic nebulizer which makes the solutions into aerosol. The aerosol was transported to the substrate by high-purity nitrogen gas and the substrate temperature was kept at 350°C. The clean substrate with a suitable mask was put on the subsector of the heater. The distance between the tip of the nozzle and the surface of the glass substrate were kept constant at 5cm. Before supplying the compressed air, the substrate temperature was to be kept at a level slightly higher than the required substrate temperature because at the onset of spraying a slight fall of temperature is likely. When compressed air was passed through at constant pressure (0.5bar), 0.6ml precursor volume, 2000μL/hr flow rate and voltage of 5-20kV, a fine Zn_{1-x}Cu_xO was produced and automatically carried to the reactor zone where film was deposited on the heated substrate. The deposition time lasts for 15min and the thickness of the films was about 500nm to 800nm. The precursor was then loaded onto the spray pyrolysis deposition system with five different doping concentrations of 0, 5, 10, 15, and 20%. After the deposition, the deposited films were allowed to cool down to room temperature and annealed before been taken out for characterization. Equation (1) give the possible chemical reaction in the formation on a substrate of ZnO:Cu thin films:



2.3 Morphological Characterization of ZnO:Cu Thin Films

Surface morphology of ZnO:Cu samples was observed by scanning electron microscope (SEM) (EVO I MA10) at an operating voltage of 20kV. The samples were gold coated before SEM investigation to study the surface morphology.

2.4 Optical Characterization of ZnO:Cu Thin Films

The optical behaviors of the thin films was investigated using a double beam UV spectrophotometer (UV-1601, PC Shimadzu). Measurements were made by placing the samples in the incident beam and another empty glass substrate in the reference beam of the instrument. The optical absorption spectra of the film with respect to glass substrate were than taken for wavelength range 230nm to 1100nm.

2.4.1 Absorbance

The absorption of radiation by any medium occurs through the excitation of electrons and photons. The absorption coefficient (α) of the thin films was estimated in accordance to the Beer-Lambert relation:

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{T} \right) \quad (2)$$

111 Where, d is the film thickness, and T is the measured transmittance.

112 2.4.2 Transmittance

113 The transmittance T is calculated from absorbance A by the following formula:

$$T = 10^{(2-A)} \quad (3)$$

114 If the films are with thickness d considerably lower than the thickness of a transparent substrate, the
115 minima ($T_{\min}$) and maxima ($T_{\max}$) of the transmission curves can be used as expressed in equation (4)
116 and (5):

$$T_{\min} : nd = \frac{\lambda}{4} (2m + 1) \quad (4)$$

$$T_{\max} : nd = \frac{\lambda}{4} (2m + 2) \quad (5)$$

117 Where, n is the refractive index of ZnO, λ is the wavelength of the adjacent maxima and minima, and
118 m is the order of the interference minima and maxima ($m = 1, 2, 3, \dots$).

119 2.4.3 Reflectance

120 The reflectance (R) is calculated from transmittance (T) and absorbance (A) using the expression in
121 equation (6):

$$R = 1 - T - A \quad (6)$$

122 2.4.4 Refractive Index

123 One of the most important optical constants of a material is its refractive index, which in general
124 depends on the wavelength of the electromagnetic wave, through a relationship called dispersion. In
125 materials where an electromagnetic wave can lose its energy during its propagation, the refractive
126 index becomes complex. The real part is usually the refractive index (n), and the imaginary part is
127 called the extinction coefficient (k). The refractive index was calculated using the reflectance (R) by
128 the following formula:

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (7)$$

129 2.5 Electrical Characterization of ZnO:Cu Thin Films

130 A QUADPRO-301-6 four point probe was used to measure the sheet resistance and the resistivity of
131 the deposited films after which the conductivity was determined from the resistivity. The sheet
132 resistance (R_s) was expressed as:

$$R_s = 4.53 \times \frac{V}{I} \quad (8)$$

133 Where, V is the measured voltage between the two inner probes and I is the current that passed
134 through the outer probes. The resistivity was computed from the relation:

$$\rho = R_s \times d \quad (9)$$

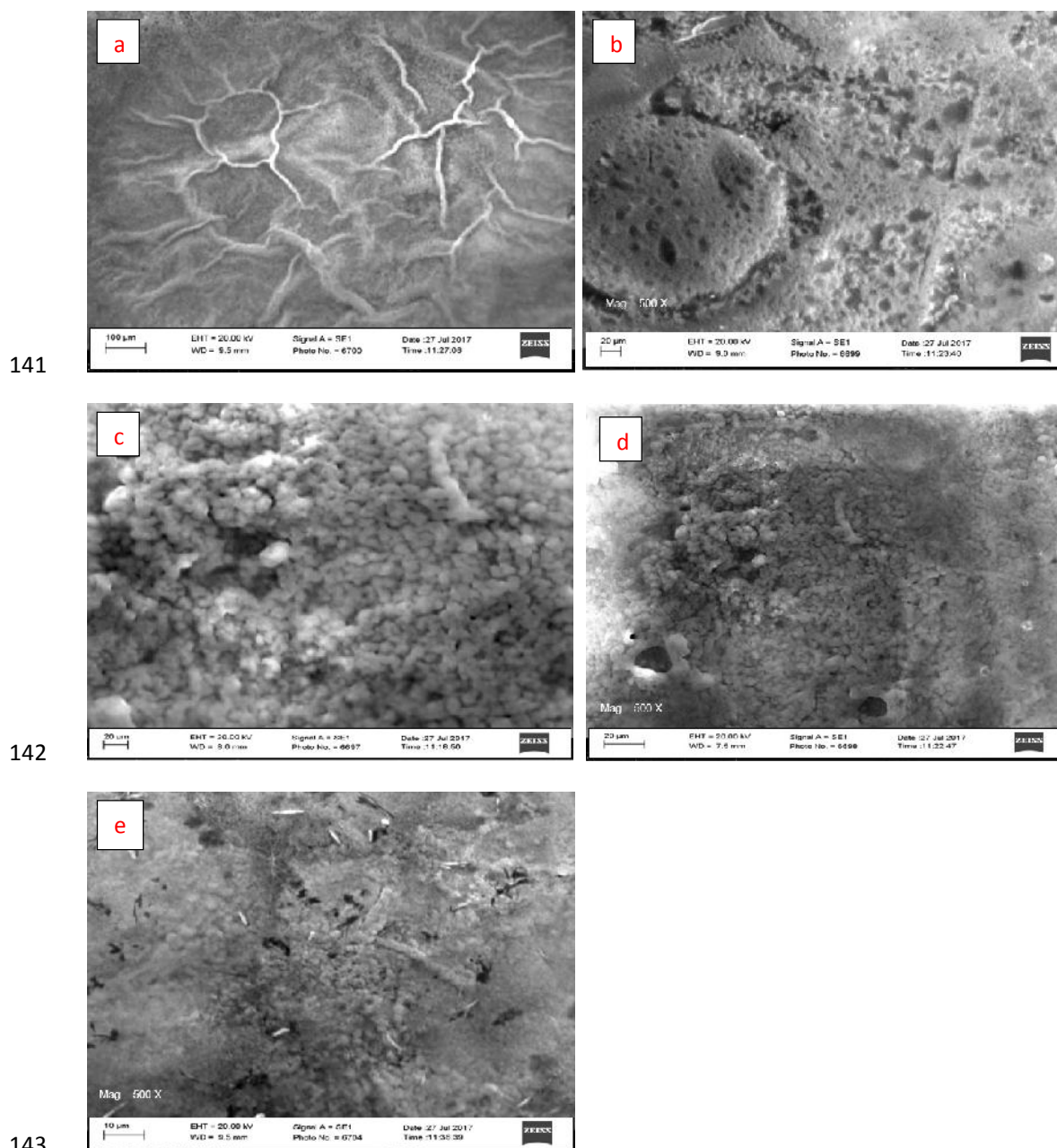
$$\sigma = \frac{1}{R_s d_c} \quad (10)$$

135 Where, d_c is the thickness of the conducting layer, ρ is the resistivity, σ is conductivity.

136 3. RESULTS AND DISCUSSION

137 3.1 Surface Morphology

138 The morphological characteristics of undoped and Cu doped ZnO thin films deposited on glass
139 substrate were observed at various percentage doping concentrations of 0, 5, 10, 15 and 20% as
140 illustrated figure 1 (a - e).



144 Fig. 1. SEM images of (a) undoped (0%) ZnO; (b) Cu doped ZnO (5%); (c) Cu doped ZnO (10%); (d)
145 Cu doped ZnO (15%); (e) Cu doped ZnO (20%) thin films.

146 Figure 1 (a) indicates the SEM micrograph of undoped ZnO thin films, and it reveals that the film is
147 uniform and nanofiber structure appear around the nucleation centre of the as-deposited ZnO thin
148 film. This may be attributed to the formation of ZnO thin films at relatively low substrate temperature of
149 350°C (Islam and Podder, 2009; Llicana et al., 2006). Due to interstitial holes of ZnO filled with

copper, most of the fiber were broken and transform into grain as the doping concentration increased to 5% (figure 1b). After the 5% doping all the fiber has broken and were transform into grain (figure 1c). The size of grain decreases with the increase of Cu in 15% doping concentration. Interestingly at 20% Cu, a combination of large and small grains were observed (figure 1d). This observation is attributed to the diffusion of Cu into ZnO which possibly causes the formation of complex centres and also likely that Cu atoms are interstitial in the ZnO lattice creating structural deformations, and thereby affecting the morphological properties of ZnO significantly.

3.2 Optical Properties

Optical properties of pure and Cu doped ZnO thin films such as transmittance, absorbance, reflectance, and refractive index were calculated on as-deposited films.

3.2.1 Absorbance

The UV-Visible absorption spectra for un-doped ZnO and Cu doped ZnO thin films with the various doping concentrations are shown in figure 2.

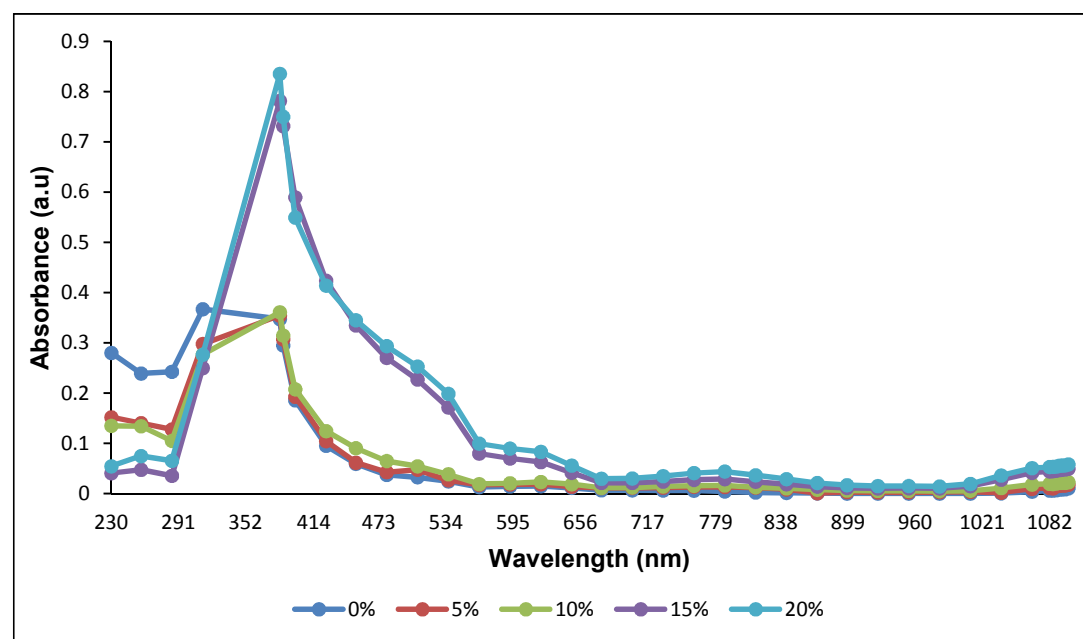


Fig.2. Variation of absorbance with wavelength of pure and Cu doped ZnO thin films at 0, 5, 10, 15, and 20%.

The above figure illustrates the variation of absorbance with wavelength of pure and Cu doped ZnO thin films. It was observed that the absorbance experience rapid increase at lower wavelengths as the doping concentration level increases. This revealed that, beyond the band edge the absorbance is very small and the transmittance is high, which illustrates that the obtained thin films are of low impurities. The reduction of absorbance in Cu doped samples for higher wavelengths can be explained as due to the removal of defects and disorder in the as-deposited film by Cu doping.

3.2.2 Transmittance

The UV-Vis transmission spectra of as-synthesized ZnO:Cu onto glass substrates with doping concentrations 0, 5, 10, 15, and 20 is illustrated in figure 3.

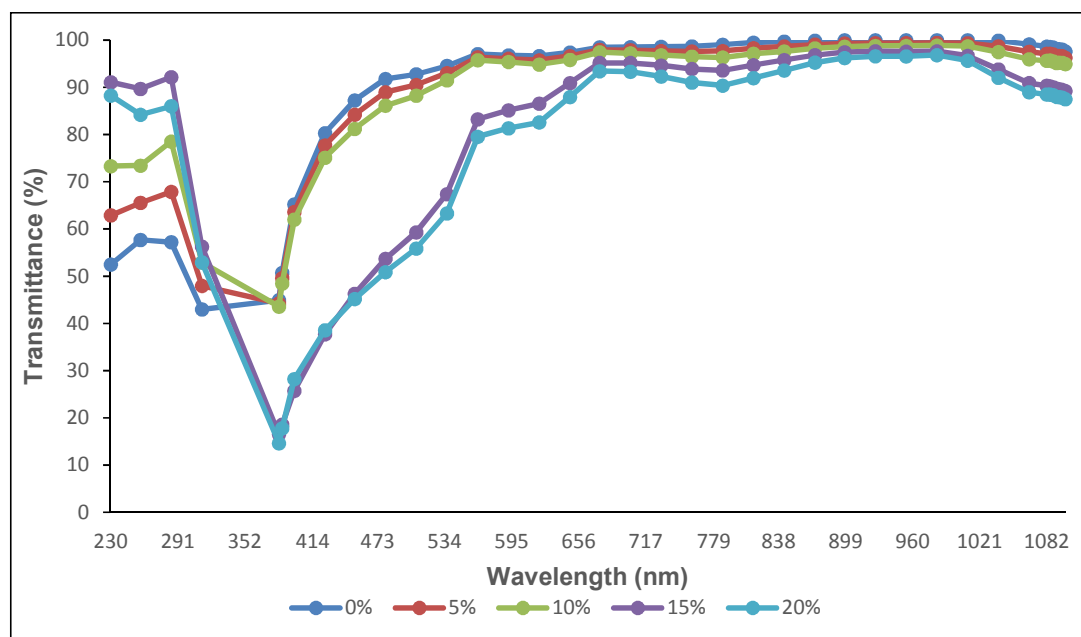


Fig.3. Variation of transmittance with wavelength of pure and Cu doped ZnO thin films at 0, 5, 10, 15, and 20%.

Figure 3 shows the transmittance of Cu doped ZnO thin films with different Cu concentrations at wavelengths from 230nm - 1100nm. It is seen that the value of transmittance decreases sharply with increasing wavelength near the ultraviolet region reaching a minimum at wavelength (~383nm) due to the band gap absorption. The transmittance then increases for wavelengths up to 700nm after which it is relatively constant. The transparency of the thin film indicates a decreasing tendency with increasing Cu concentration and the surface roughness. The flat aspect of the transmission curve without interference fringes emphasizes the surface homogeneity with small crystallite size. The average value of transmittance decreases from about 95% to 75% as the dopant concentration increases. This can be attributed to the incorporation of Cu^{2+} ions which replaces the substitutional or interstitial Zn^{2+} ions from the host lattice. This incorporation of Cu^{2+} ions produces stresses in the films which causes the structural deformation or defects in the thin films. This will in turn increase the photon scattering from the defects (Znaidi, 2010). For higher doping levels, the samples were found light to deep silvery in colour and less transparent to naked eye.

3.2.3 Reflectance

Figure 4 indicates the variation of reflectance with wavelength of pure and Cu doped thin films.

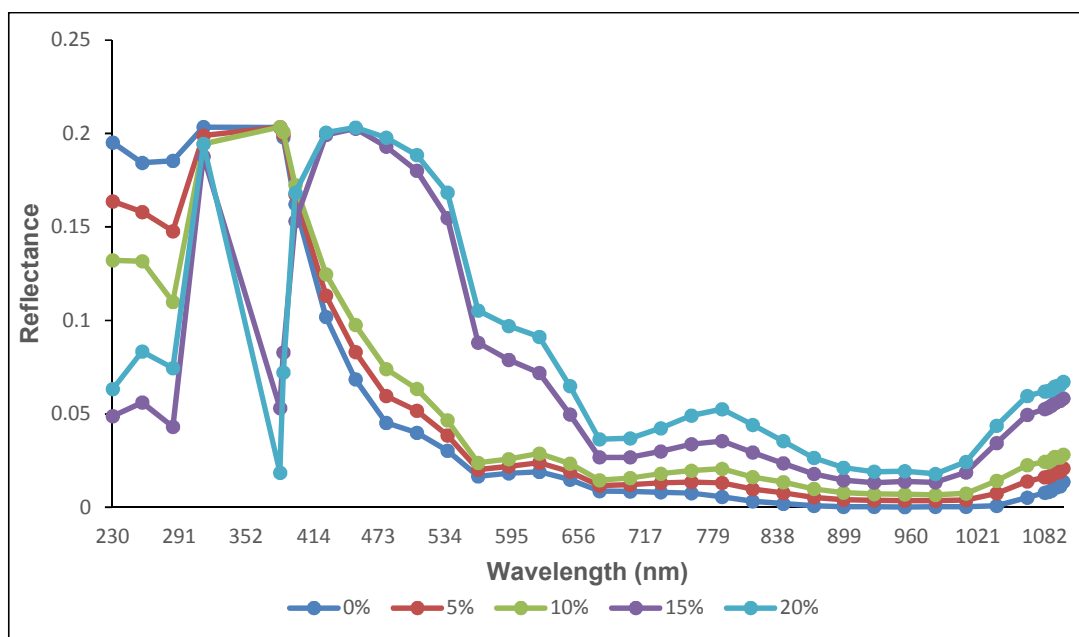


Fig.4. Variation of reflectance with wavelength of pure and Cu doped ZnO thin films at 0, 5, 10, 15, and 20%.

It was observed that the absorption slightly decreases as the wavelength increases. The reflectance increases with increasing doping concentration level in the wavelength range of 313nm to 560nm, then decreased as the wavelength increases. Also, it was revealed that the sample got silverer in color as the level of doping increases, which is a visual manifestation of increase reflectance with increasing level of doping.

3.2.4 Refractive Index

The refractive index of the films has been calculated from the transmission spectra using equation. The variations of refractive index (n) for pure and Cu doped ZnO thin films with Cu doping is shown in table 2 and these are graphically shown in figure 5.

Table 2. Average refractive indices of pure and Cu doped ZnO at various concentrations of 0, 5, 10, 15, and 20%.

Sample code	Refractive index (n)
CuZnO ₀	1.4597
CuZnO ₅	1.5032
CuZnO ₁₀	1.5405
CuZnO ₁₅	1.6996
CuZnO ₂₀	1.7865

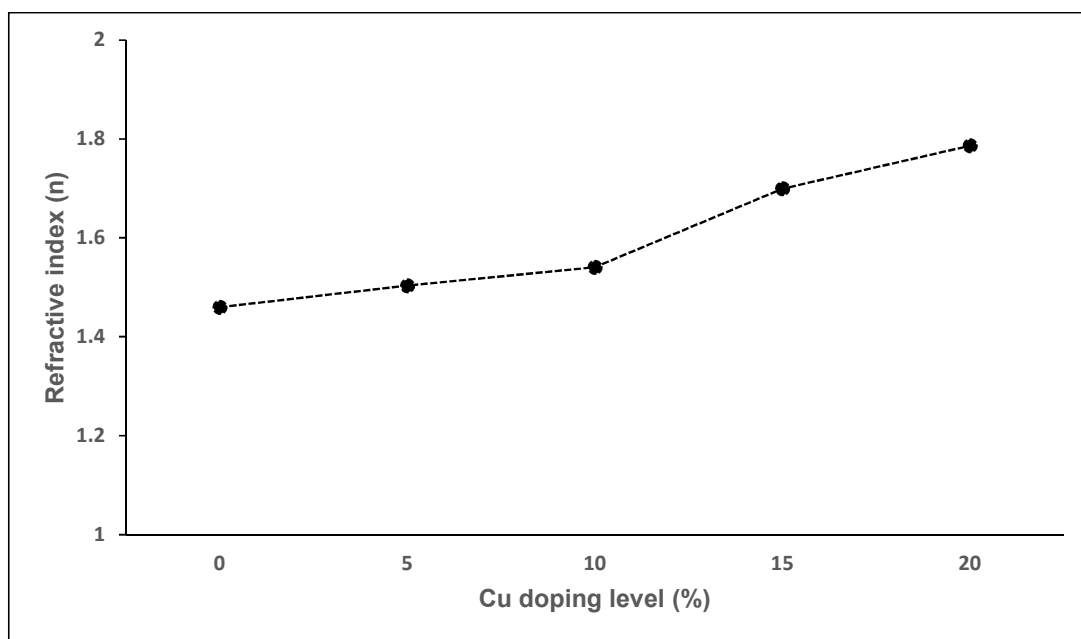


Fig. 5. Variation of refractive indices of pure and Cu doped ZnO thin films at 0, 5, 10, 15, and 20% concentrations.

The refractive index is determined by computing the transmission and reflection data. The refractive index of the film significantly changes with the deposition parameter. It shows that the refractive index increases with increasing concentration of Cu doping.

3.3 Electrical Properties

3.3.1 Resistivity

Resistivity of the ZnO and Cu doped ZnO thin films have been measured by four-probe method as shown in figure 6.

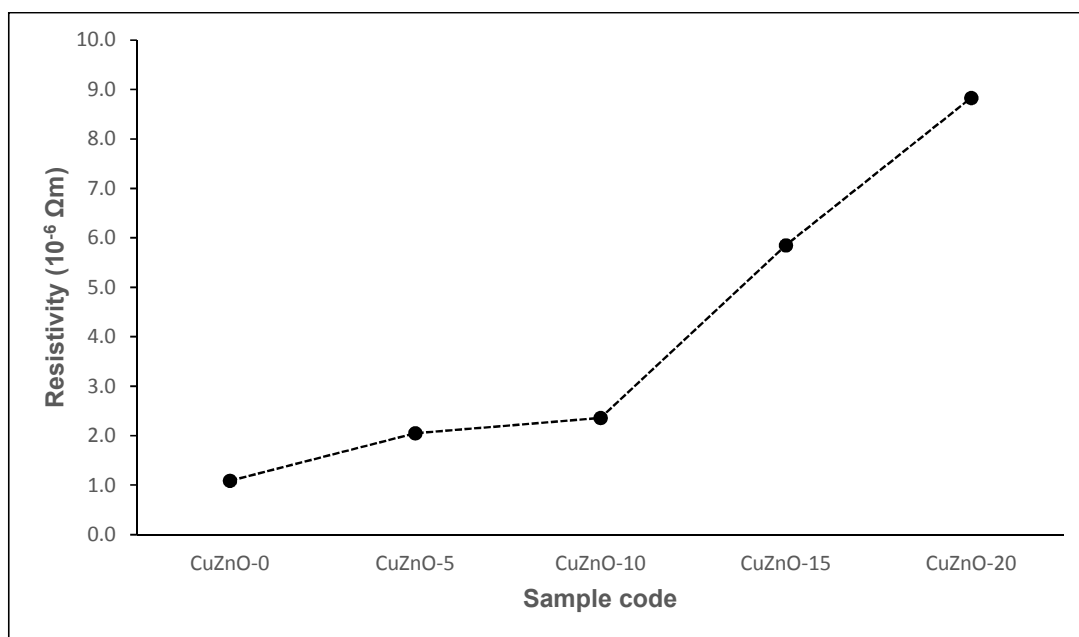


Fig. 6. Resistivity of ZnO and composite Cu:ZnO thin films with various concentrations.

Figure 6 shows that the electrical resistivity increases with the increases of Cu concentration. The high electrical resistivity of ZnO films is because of the chemisorption of oxygen at grain boundaries which is possible since the carrier gas used during deposition was ambient air. The four co-ordinated Zn, Cu and Cu cations have ionic radii of 0.06, 0.06 and 0.057nm respectively, with stable electronic configuration, Zn^{2+} ($3d^{10}$), Cu^{2+} ($3d^9$) and Cu^+ ($3d^{10}$). Diffusion at high firing temperature may lead defect reactions in which Cu^{2+} cations substitute Zn^{2+} cations in the wurtzite unit cell of ZnO. The stability of the coulomb forces of the interactions between the acceptor defect and intrinsic ZnO donors may occur by capture of an electron from the lattice.

3.3.2 Conductivity

The variations of electrical conductivity with temperature for as-deposited Cu:ZnO thin films are shown in figure 7.

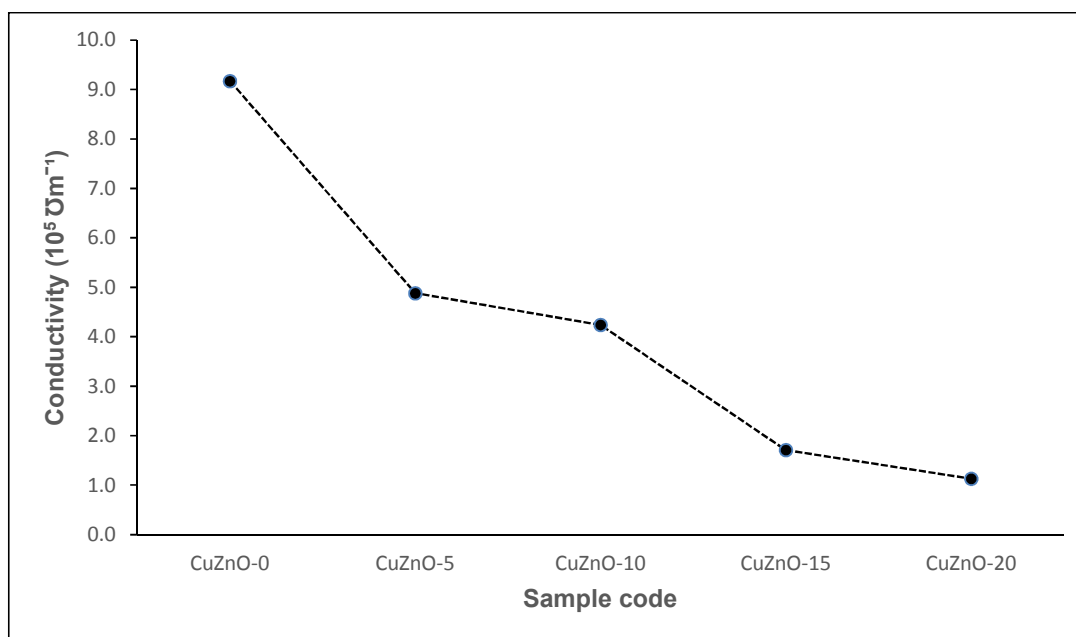


Fig. 7. Conductivity of pure ZnO and composite Cu:ZnO thin films with various concentrations.

This type of variation indicates the semiconducting behavior of the films. The electrical conductivity decreases with the increasing of the film concentration (Lee et al., 2004). Incorporation of Cu into ZnO reduces its conductivity as Cu introduces deep acceptor level and it traps electrons from the conduction band.

4. CONCLUSION

Thin films of different doping concentrations of Cu were deposited on glass substrate keeping the substrate temperature at $350^{\circ}C$. SEM micrograph shows that all the films are found well covered on the glass substrate and sprayed particles are well adhered to the glass substrates. Due to interstitial holes of ZnO are filled with copper, most of the fiber broke and transformed into grain at 5% Cu doping concentration. The size of grain decreases with the increase of Cu in 15% doping concentration. Interestingly, at 20% Cu, a combination of large and small grains is observed. Absorbance decreases with higher percentage of Cu concentration. These spectra show high absorbance in the wavelength range from 230nm to 400nm. The value of transmittance is high in the visible and infrared regions but minimum in the ultraviolet region. These spectra show high transmittance near about 75% - 95% in the wavelength range from 400nm to 1100nm. The increase in the Cu incorporation in the film results in the overall increase in the refractive index.

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