



RESEARCH ARTICLE - PHYSICS

Investigating the Structural and Optical Properties of Pure and Zinc (Zn)-Doped Copper Oxide at Different Weight Ratios

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Article Info.	Abstract
<p><i>Article history:</i></p> <p>Received 07 March 2024</p> <p>Accepted 21 April 2024</p> <p>Publishing 30 September 2024</p>	<p>This study explores the effect of zinc (Zn) doping on the structural and optical properties of the copper oxide. Nano crystalline copper oxide (CuO) thin films were deposited onto the glass substrates by using a plasma deposition technique. This CuO was then doped with Zn ions at certain weight percentages. The structural and morphological characteristics of both pure and Zn-doped CuO thin films were examined by using X-ray diffraction analysis, field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and UV optical spectrometry. From XRD, it was revealed that all thin membranes exhibit multi-crystallization and the crystalline volume of thin films was calculated using Scherrer's formula. The crystal size of the Zn doped CuO changed when compared to the pure CuO due to the Zn size, density strain of CuO lattices and dislocation density. From the results of the FESEM and AFM, presence of the small, spherical-shaped granules in the thin films of pure CuO revealed. However, post-doping results revealed the presence of greater homogeneity in the CuO resulting in a regular granular nature. Furthermore, results of the optical study corroborated the successful doping of the CuO as pure CuO possess highest optical absorption values and the lowest values of the optical band gap. However, post doping results of the CuO showed an increase in optical band gap when the doping rates was less than 6% but shows decrement at relatively higher doping rates revealing the effect of Zn doping on CuO.</p>

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1. Introduction

Nowadays, research on metal-doped transition metal oxides and nanostructured metal oxides is drawing researcher's attention [1]. Among different metal oxides, CuO and Cu₂O are commonly used oxides for the preparation of nanoparticles of various sizes and shapes. The properties of these nanostructures depend on the preparation methods and the crystal structure thus obtained [2]. Consistent with literature, variety of synthesis methods have been reported for the preparation of CuO nanostructures including thermal evaporation [3], sonochemical synthesis [4], sol-gel method [5], chemical vapor deposition, laser ablation, and microwave-assisted synthesis [6][7]. Copper oxides are considered an important semiconductor and are being studied as a p-type semiconductor metal with a bandgap of about 1.7 eV [8]. These oxides find extensive uses in variety of applications including solar cells [9], gas sensing [10] and biosensors [11] due to their easy accessibility, low processing cost, non-toxic nature, and good thermal stability.

The conduction properties of the nonconductive materials directly depend on the band gap that can be controlled by doping/adding impurity ions such as Zn, Cr, or Ni, etc. to the host material. This doping effect helps to modify the electrical, optical and magnetic properties of the base material. Among the aforementioned dopants, the most widely used dopant is zinc (Zn). It is considered as one of the most effective dopants for copper oxide because the ionic radius of zinc (0.6Å) and copper (0.57Å)

are close to each other that results in efficient incorporation of zinc ions into the CuO lattice without affecting its crystal structure [12]. Many researchers have studied the effect of doping on the structural and optical properties of CuO as Jayaprakash et al. [13] reported a decrease in the band gap after doping with zinc ions. Similarly, in another study by Rejith et al. [14], the effect of Zn doping on the properties of the CuO nanoparticles was studied. Keeping in view the above discussion, this study aimed (i) to synthesize thin films of pure and doped copper oxide (CuO) by radio-frequency plasma deposition technology and (ii) to investigate the effect of zinc (Zn) doping on the structural and optical properties of the pure copper oxide.

2. EXPERIMENTAL DETAILS

Herein, a thin film of pure CuO and zinc-doped CuO was deposited on a clean glass substrate using the magnetron sputtering process at a temperature of 350 °C. Tablets of Pure copper oxide and also zinc-doped copper oxide was used in different proportions as spray targets with a diameter of 5cm and a thickness of 3mm with a flow of argon and oxygen gases (as reactive gasses) at a mixing ratio of 1:7 inside the deposition chamber. The distance of the target from the substrate was maintained at approximately 10 cm. Afterwards, the glass substrates were cleaned with soap and water, followed by drying, and dipping in chromic acid for 24 hours. This was followed by washing it again first with deionized water and then with acetone, and heated in ultrasound waves. Afterwards, the chamber was first emptied of air followed by pumping in the argon and oxygen gases at the pressure of 2.5×10^{-2} torr before deposition. The target power was maintained at about 100 watts, and the deposition time was set to 2 hours. After sample deposition, the crystal structure of the resulting materials (pure and doped) was then studied through XRD analysis. Field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) were also used for morphological/ topographical analysis of the synthesized materials. Furthermore, UV-visible spectrophotometer was used for the optical analysis of the materials.

3. RESULTS & DISCUSSIONS

3.1. Crystallographic analysis

Crystallographic results of the pure and doped (12% zinc doping) CuO thin films are represented in Figure 1a-b and Table 1-2 respectively. The results of the study revealed that the films examined are a mixture of tenorite crystallised CuO phases and poly-crystalline cubic Cu₂O phases. The two peaks located at 2θ of 42.5° and 62.2° belong to the (200) and (220) planes of Cu₂O, respectively (JCPDS77-0199). For CuO, there are two main peaks that appear at 2θ of 35.4° and 37.8° with reflections of (002), (111) and 5 small peaks at 47.35° , 52.7° , 56.3° , 68.35° and 73.7° with reflections of (-202), (312), (021) (-113), 004), respectively. According to JCPDS, the intensity of the peaks for CuO increased with Zn doping. It was observed that the improved CuO growth along the trend (111), (002) It occurs at the expense of Cu₂O. In addition, raising the temperature of the substrate to a level 350 °C leads to the instability of the Cu₂O phase and the films of different phases were obtained [15].

Table 1. Crystallite size, dislocation density and strain value of pure CuO films obtained by XRD

Material type	2 Theta peaks (2θ)	FWHM	D (nm)	d-spacing [Å]	dislocation density $\delta * 10^{-3}$ (nm ⁻²)	strain across $(\epsilon) * 10^{-3}$	Grain size rate (nm)
CuO undoped	33.0083	0.24	33.1480	2.7115	0.9101	3.5343	26.8558
	35.3739	0.36	21.9588	2.5272	2.0739	4.9258	
	38.4956	0.96	8.1600	2.3366	15.0184	11.9963	
	42.0553	0.18	43.0268	2.1467	0.5402	2.0431	
	56.3945	0.48	15.2348	1.6302	4.3085	3.9065	
	67.0456	0.18	38.4291	1.3947	0.6771	1.1856	

Table 2. Crystallite size, dislocation density and strain value of Zn-doped CuO films obtained by XRD.

Material type	2 Theta peaks (2θ)	FWHM	D (nm)	d-spacing [Å]	dislocation density δ * 10 ⁻³ (nm ⁻²)	strain across (ε) * 10 ⁻³	Grain size rate (nm)
(CuO:Zn)12%	35.4813	0.6	13.1713	2.5279	5.7642	8.1832	21.2614
	37.2087	0.36	21.8438	2.4145	0.9371	3.0214	
	38.2314	0.24	32.6660	2.3138	1.4702	3.7077	
	43.3483	0.72	10.7094	2.0846	8.7191	7.9049	
	57.0669	0.3	24.2985	1.6126	1.6937	2.4075	
	67.7115	1.2	5.7421	1.3826	30.3293	7.8050	

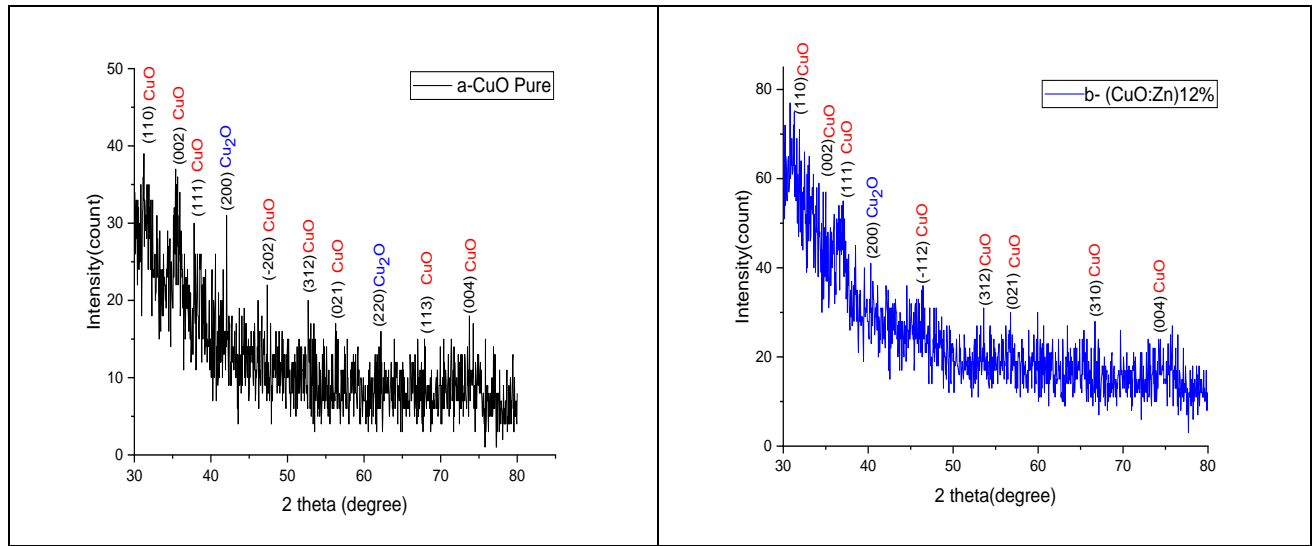


Figure 1(a-b). XRD results of (a) pure and (b) Zn doped CuO films.

From the results obtained in Table 1 for CuO films deposited on glass substrates at a temperature of 350°C, the XRD reflections indicate that the lattice parameters were determined using eight reflection lines, where the size of the crystals was calculated using the Debye-Scherrer equation [16] for copper oxide films deposited with radio frequencies.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where k is 0.9 for the spherical shape that is considered the least distant, (λ) is the wavelength of the X-rays and (β) is the full width of the half-maximum of the peak and (θ) is the Bragg angle, and the dislocation density was calculated to determine defects in the lattice and micro strain using Eq

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

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

Where, δ refers to the micro-strain and ε is dislocation density.

Results of the XRD analysis revealed that the positions of the XRD peaks shifted slightly towards the right side after doping with zinc. Substituting Zn does not generally change the lattice constants of CuO, but may lead to stress, shrinkage, anisotropy and thus distortion of the lattice. Therefore, compressing stress shifts the diffraction levels to higher angle values [17]. This slight change in the diffraction angles is due to the microscopic structure as well as the crystalline size of the nano-copper saturated with Zn, which depends on the doping ratio, as increasing the doping of the zinc led to an increase in the intensity of the peaks at the (111) (002) levels as corroborated in Figure 1a-b. However, no linear dependence with increasing zinc concentration in the lattice was observed [19], because the ionic radius of zinc is nearly 0.6 Å, which is close to the ionic radius of copper i.e., 0.57 Å. Furthermore, it was observed that the size of the crystals decreased with increasing concentration of zinc doping, while the strain increased with the increased zinc ions pressure in the lattice. This led to an obstruction in the growth of the CuO crystal leading to a decrease in the size of the crystals. While on the other hand, at lower zinc concentration, the size of the crystals increases with the decrease in strain leading to the deformation of the network due to stress as a result of the anisotropic contraction of the network.

3.2 FE-SEM and AFM

Through microscopic FESEM results of CuO (Figure 2), it was observed that the copper oxide contains a mixture of atoms having spherical shape with an unequal grain size of between 7-50 nm. This is due to the variable growth properties of the CuO crystal with a monoclinic structure consisting of oxygen and copper [18].

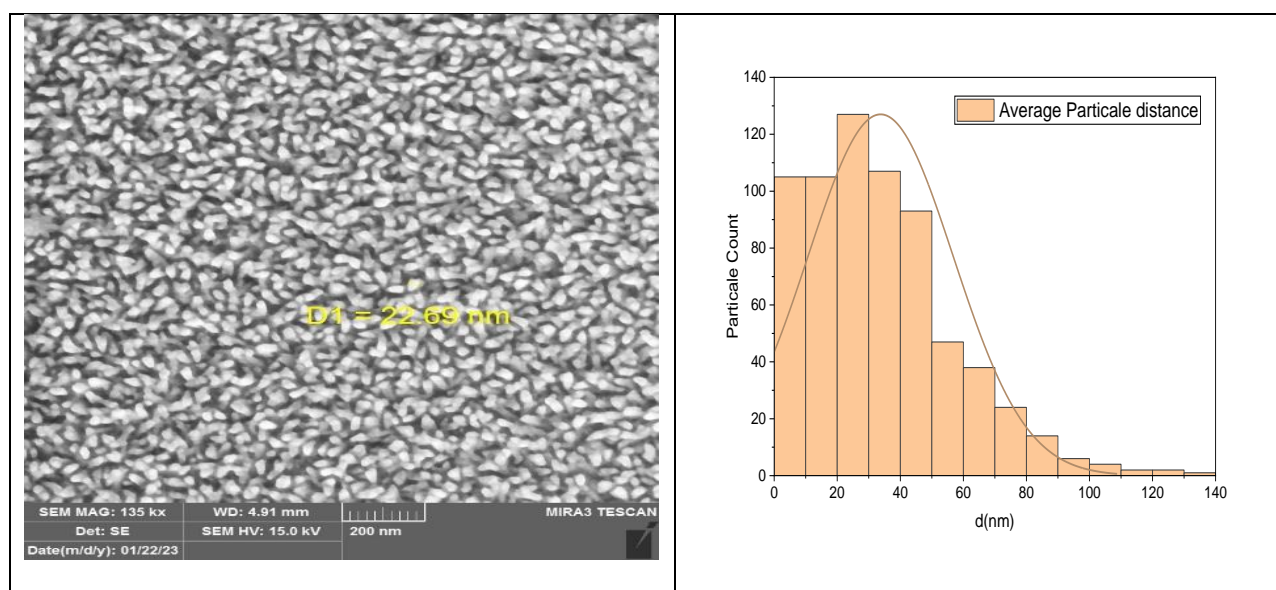


Figure 2. FE-SEM images of pure CuO films.

Zn doping to CuO (Figure 3), however, has little effect on CuO morphology. However, the inspection of the FESEM data demonstrates how the Zn doping causes a variation in the size of the CuO particles, leading to the production of tiny nanostructures. Doping with Zn will determine the dimensions and shape of the CuO nanostructure. In Figures 2-3, the uniform growth of uniform dispersed single copper oxide crystal was observed with a reduction in the grain size due to tensile stress. Results of the study correlate with already reported literature [17].

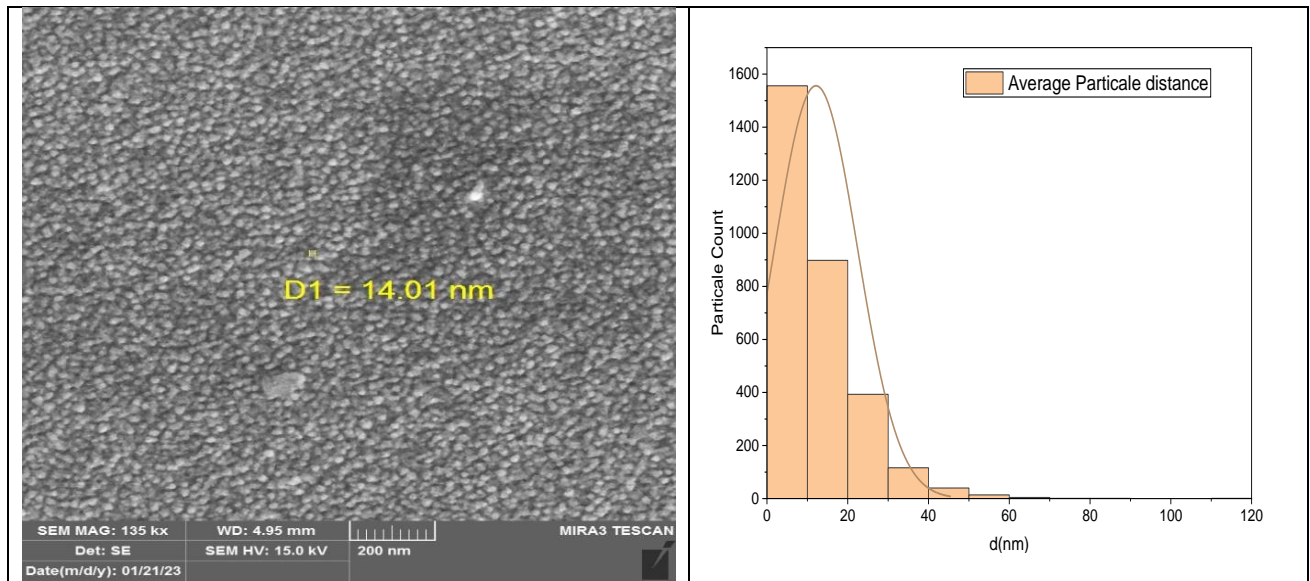


Figure 3. FESEM images of the Zn doped CuO films.

Microscopic AFM images of the pure copper oxide (Figure 4) revealed the formation of semi-spherical, nano-sized particles whose distribution is irregular. The surface area relative to volume and high surface energy are responsible for the aggregation.

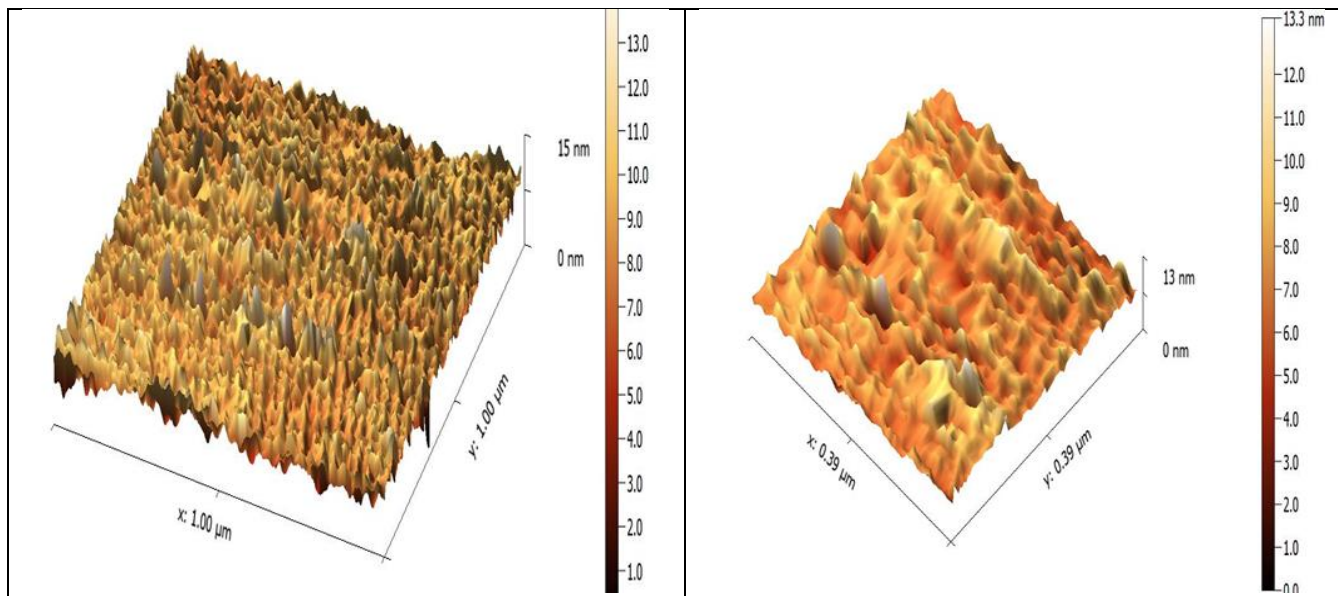


Figure 4. AFM results of pure CuO films.

However, after Zn doping to copper oxide, the crystalline growth of nanomaterials affected to a greater extent. It is also possible to control the surface morphology of CuO doped with zinc, which is greatly affected by the presence of other ions [19][20], where zinc acts to smoothen the CuO surface in the CuO:Zn nanocomposite. However, too much high concentration of zinc ions reduces the surface energy through collection.

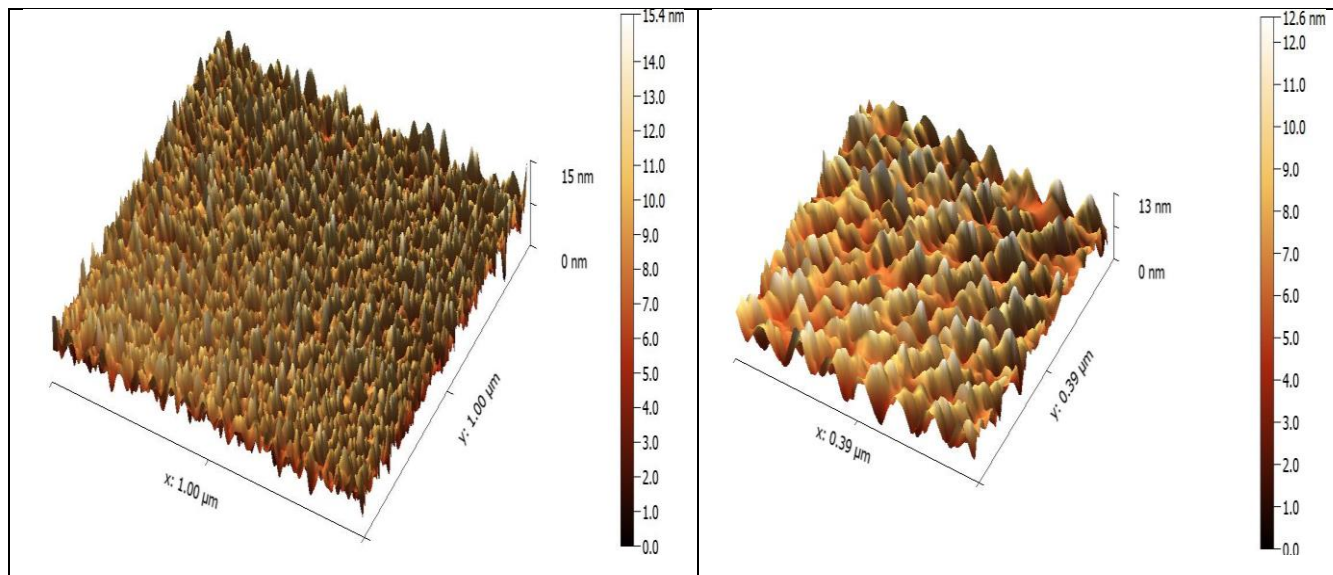


Figure 5. AFM images of Zn doped CuO films.

The optical properties including absorbance, transmittance, reflectance, and absorption coefficient and band gap; of pure as well as Zn doped CuO thin films were studied to investigate the effect of Zn doping to the properties of the copper oxide films. Results of the study (Figure 6a) of the absorbance measurements clearly revealed the inverse relation between absorbance and the implantation dose. While on the other hand, Figure 6b suggests that the pure CuO possess low transmittance when compared with the optical transmittance values of the Zn doped CuO in the visible region. It was found that the highest value comes nearly to 10% when the Zn doping percentage was 12% in the visible range. The increase in optical transmittance of the doped material was mainly due to the crystalline nature of the thin films. These changes are consistent with the physical properties of the thin films being studied.

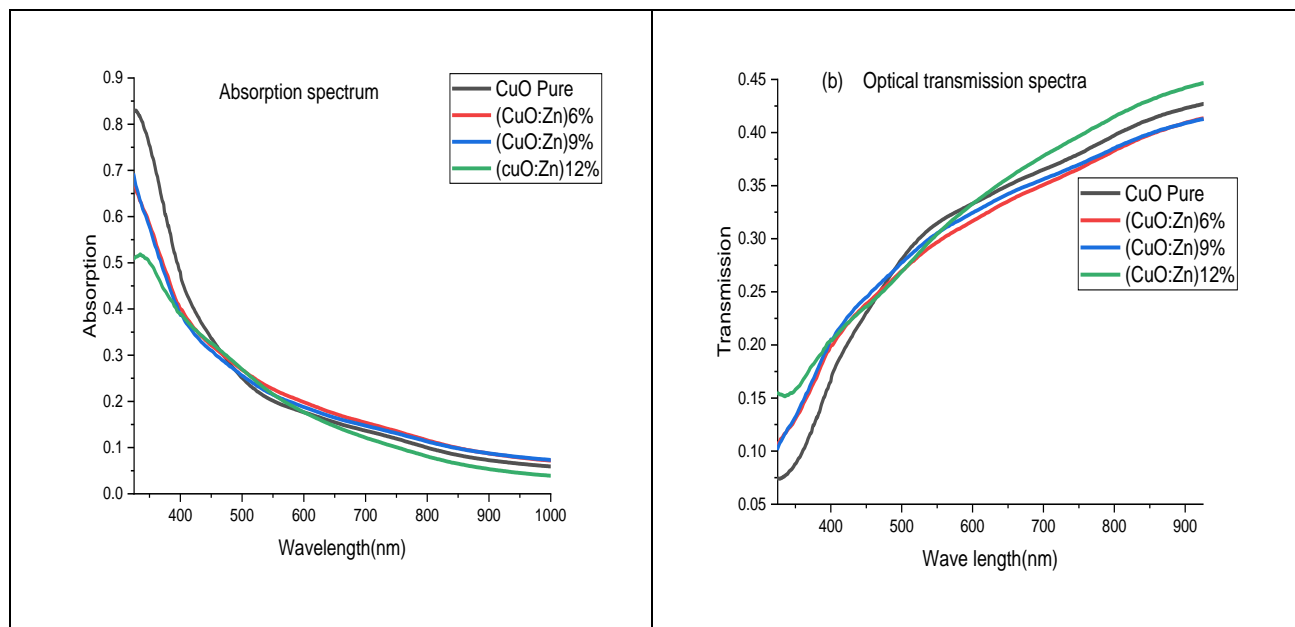


Figure 6a-b. The relationship between (a) absorbance (b) transmittance against wavelength for pure and doped copper oxide films.

Figure 7a shows the reflectivity of the synthesized materials (both pure and doped CuO) as a function of wavelength revealing that the reflectivity increases with an increase in short light wavelengths. However,

reflectivity increased monotonically with an increase in wavelength. Relation of the absorption coefficient of both pure and doped CuO with wavelength has been summarised in Figure 7b, the results of the study revealed that the absorption coefficient of (CuO) films doped with zinc decreases with increasing wavelength. The value of the absorption coefficient is high within the limits (10^4 cm^{-1}) suggesting the possibility of direct transfer from the valence band to the conduction band. Further, with an increase in Zn doping, the absorption coefficient creep towards the shorter wavelengths as confirmed from the decline in its value.

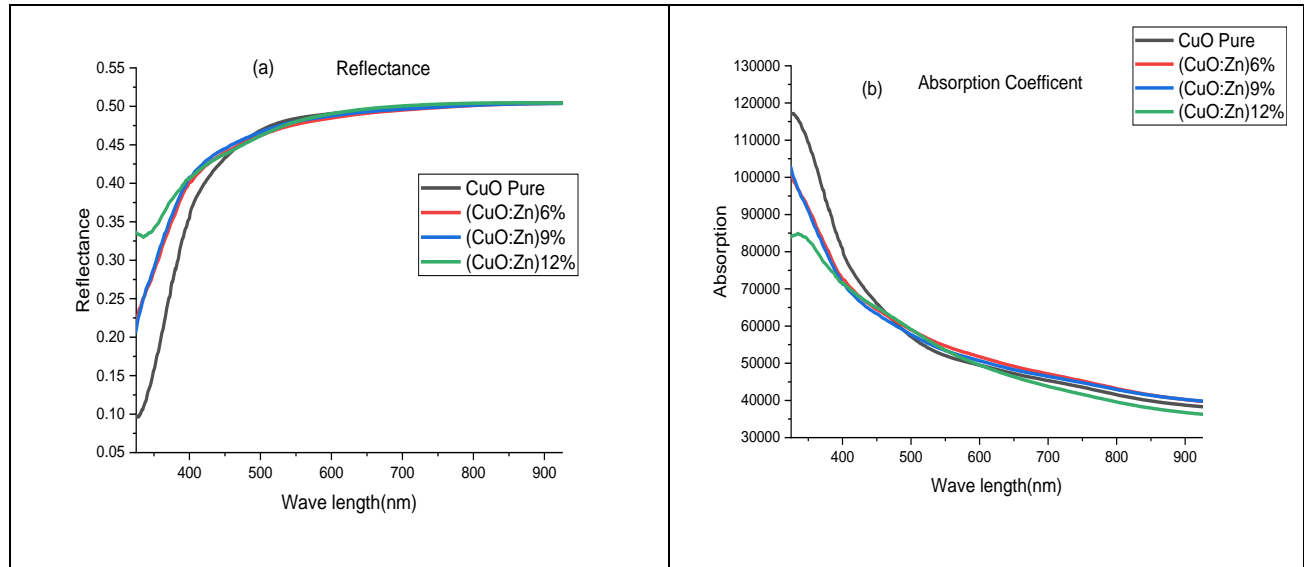


Figure 7a-b. Relationship between (a) reflectivity (b) absorption coefficient against wavelength for pure and Zn-doped copper oxide films.

The visual properties of both pure and Zn doped CuO nanoparticles are shown in Figure 8. Optical band gap for CuO particles as 2.25V. The increase in the energy gap of nanoparticles compared with its bulk counterparts (1.85V) returns to the effect of quantitative size [21] because in the case of the bulk matter, energy ranges are effectively form by combining a range of convergent energy levels for atoms. As the particles, approach the nano-volume, the overlapping of adjacent energy levels minimizes that therefore widen the width of energy band. This leads to an increase in the band gap between the parity pack and the plug pack with low particle size. Further, Zn doping to CuO resulted in a decrease of (E_g) to 2.10 eV and the effect can be compounded as a result of the transition from the oxygen 2p state to d state of Cu and Zn. Overall, the results of the study revealed that the doping of CuO with Zn helps in improving the optical properties of the CuO when compared with the pure CuO and this improvement in optical characteristics is highly dependent on the concentration of Zn ions used for doping [22].

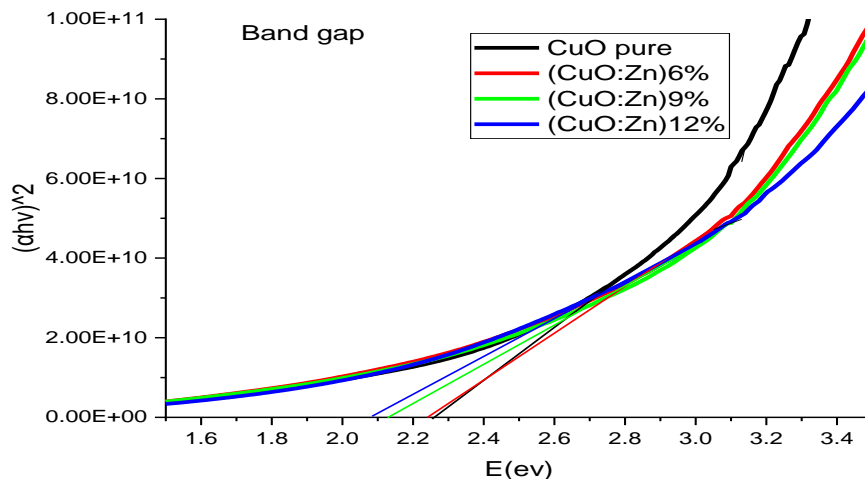


Figure 8. The relationship between $(\alpha h\nu)^2$ and photon energy for pure and Zn-doped CuO films.

4. Conclusions

Herein, pure and Zn doped CuO thin films were synthesized by using radio-frequency plasma deposition technology and the variation in the structural and optical behaviour of CuO was investigated both before and after Zn doping. XRD characterization revealed that the prepared films are poly crystalline in mixture of tenorite crystallised CuO and Cu₂O phases. The intensity of the peaks for CuO increased with the doping of zinc. Zn-doped CuO crystal size is highly dependent on the proportion of Zn used for doping as the size of particles reduced due to the replacement of Cu²⁺ ions with Zn²⁺ ions. Further, FESEM analysis also revealed that the size and shape of the doped CuO particles depends mainly on the concentration of zinc in the lattice. Doping of CuO results in making the membrane surface more homogeneous and regular in comparison to the pure CuO films. Additionally, the study of the optical properties of the prepared samples also revealed that increasing the concentration of zinc leads to a decrease in the band gap, and thus improving the electrical conductivity of the material that make them efficient for use in solar cells and optical devices.

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6. References

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