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Study of the Optical Properties and Structure of in Thin Films Copper Oxide Doped with Zinc Oxide

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Abstract: *Nano Copper oxide doped (2,4,6,8)% (CuO) thin films were fabricated on glass slide substrates at (4000C) by spraying method using a solution containing Copper (II) oxide, Copper nitrate and water. The effect of Zinc nanoparticles (ZnO) on the structural and optical properties of (CuO : ZnO) thin films were studied, the structural properties were studied by X-ray diffraction (XRD). The results show that all the samples have a cubic structure. After (ZnO) doping, The topography properties were studied by scanning electron microscopy (SEM) while optical properties were studied by Uv-vis spectrophotometer. The optical transmittance has been decreased, the optical band gaps of (CuO) doped (ZnO)thin films decrease as the(ZnO) content increased.*

Keywords: *Thermal Spray Technique, Copper Oxide Thin Film, Structural Properties.*

Introduction

Copper oxides are semiconductors and have been studied for applications including rectifying and microwave diodes and solar cells. Cupric oxide (CuO) is a p-type semiconductor having a band gap of 1.21–1.51 eV and monoclinic crystal structure [1]. Cuprous oxide (CuO) is also a p-type semiconductor having a band gap of approximately 2.0 eV and a cubic crystal structure [1]. Of the above oxides CuO is the most studied because of its high optical absorption coefficient in the visible range and its reasonably good electrical properties [2]. Several methods have been used to prepare copper oxide thin films. These include thermal oxidation [3]; electrodeposition [4]; chemical conversion [5]; chemical brightening [6]; spraying [7]; chemical vapor deposition [8]; plasma evaporation [9]; reactive sputtering [10]; and molecular beam epitaxy [11].

Zinc oxide (ZnO) is the most interesting metal oxide semiconductor due to its large bandgap of 3.37 eV and high binding energy of 60 meV. In addition, ZnO nanostructures, such as nanorods and nanowires, have a high-surface-area-to-volume ratio, which is the most significant property of ZnO nanostructures that are used for many of applications such as gas sensor, ultraviolet detector, Light emitting diode (LED). ZnO nanorods as well as nanowires is prepared through different physical and chemical methods like CVD, electrochemical, thermal evaporation, hydro and solvothermal [12].

The average crystallite size (D) was estimated by Scherrer's equation [13], as follows.

$D = K\lambda / (\beta \cos\theta)$ …………….1

where K = 0.9 is Scherer's constant, λ is X-ray radiation's wavelength (λ = 1.54056 Å), β is the peak full width at half maximum (FWHM) in radians, and θ is the Bragg diffraction angle at which FWHM is measured.

The optical band gap energy (Eg) of the as-synthesized nanoparticles is obtained from the UVVis spectra by using the Tauc's relation [14]:

$$\alpha h\nu = A_s(h\nu - E_g)^r \text{.........................} 2$$

where α represents the absorption coefficient, hυ is photon energy, A is constant (absorbance) and the exponent n = ½ for direct transition.

Experimental

Thin films were prepared from pure copper oxide impregnated with zinc oxide using an aqueous solution of copper (II) nitrate with (0.1)molarity in de-ionized water. The solution is mixed by a magnetic stirrer for half hour and then the solution was sprayed on the glass substrates at $(400)^o$C with air as the carrier gas. In ther hand Zinc nitrate solution with (0.1) molarity was dropped into the copper (II) nitrate solution to accomplish different doping concentration (2,4,6,8)%. And then the resultant solutions were deposited on glass substrates at(400^oC)by the same procedure.

Results and discussion:

1. XRD Analysis:

Different coatings were prepared by changing the ratio of Copper oxide nanoparticles (CuO) in (ZnO) thin films. Fig.(1), Shows the XRD patterns for the samples prepared under the experimental conditions. For pure (CuO) the peaks at scattering angles (2θ) of (32.6402, 35.6999 and 38.858) corresponding to the reflection from (110), (002) and (111) crystal planes, respectively.

By increasing (ZnO) concentration, peak position is shifted toward lower values, as shown in Table (1).The X-ray of (CuO) reduces with increasing (ZnO) concentration. It may be due the increasing volume of unit cell as well as decreasing molecular weight of the samples. The strongest peak of thin films was used to determine the average crystallite size using Scherrer's equation (1).

The average crystallite size was found to Increasing from (13.026 to 16.637) nm as the concentration of (ZnO) increases from (0% to 8%).

Table 1: shows the results of (XRD) tests for thin films of Zinc oxide doped copper oxide

Sample	2θ (degree)	FWHM (radian)	C.s(nm)	d std (ºA)	(hkl)	phase	NO Card
CuO (Pure)	32.6402 35.6999 38.858	0.56 0.6213 0.6467	14.782 12.443 13.026	2.741 2.513 2.315	110 002 111	CuO CuO CuO	00-901-6105 00-901-6105 00-901-6105
CuO ZnO (2%)	22.496 35.723 38.967	1.040 0.600 0.613	7.788 13.911 13.747	3.949 2.511 2.309	110 002 111	CuO CuO CuO	00-901-6105 00-901-6105 00-901-6105
CuO ZnO (4%)	23.234 35.775 39.085	0.840 0.724 0.867	9.655 11.530 9.723	3.825 2.507 2.302	110 002 111	CuO CuO CuO	00-901-6105 00-901-6105 00-901-6105
CuO ZnO (6%)	32.875 35.877	0.810 0.800	10.226 10.438	2.722 2.501	110 002	CuO CuO	00-901-6105 00-901-6105

	39.262	0.920	9.168	2.292	111	CuO	00-901-6105
CuO ZnO (8%)	35.814	0.675	12.368	2.505	002	CuO	00-901-6105
	38.634	0.506	16.637	2.328	002	CuO	00-901-6105
	39.333	0.938	8.994	2.288	111	CuO	00-901-6105

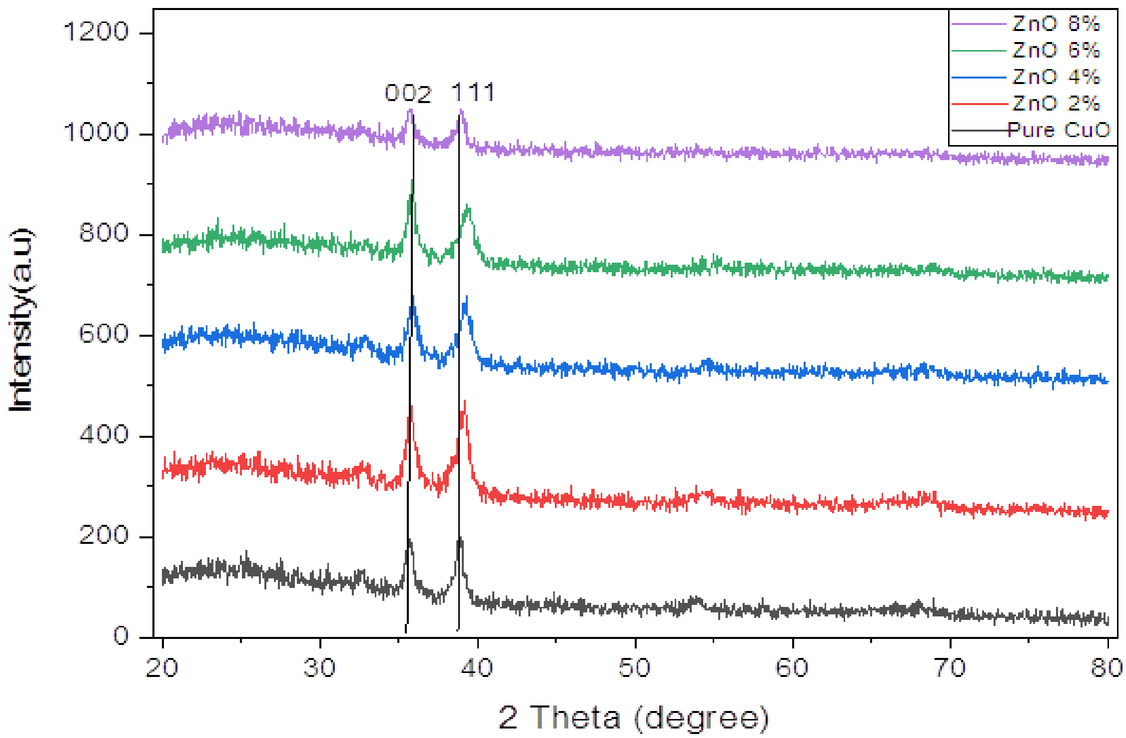

Figure 1-XRD patterns for CuO:ZnO thin films with different ratio

Optical properties

Fig. (2), shows that the transmittance spectra of nano (CuO: ZnO) thin films with different nano (ZnO) concentration. The transmittance decreases with increasing doping concentration. This continuous decreasein transmittance is due to lattice defects. The nano (CuO) may occupy interstitial site on the (ZnO)lattice and decrease transmittance of light thereby increasing the absorbance.

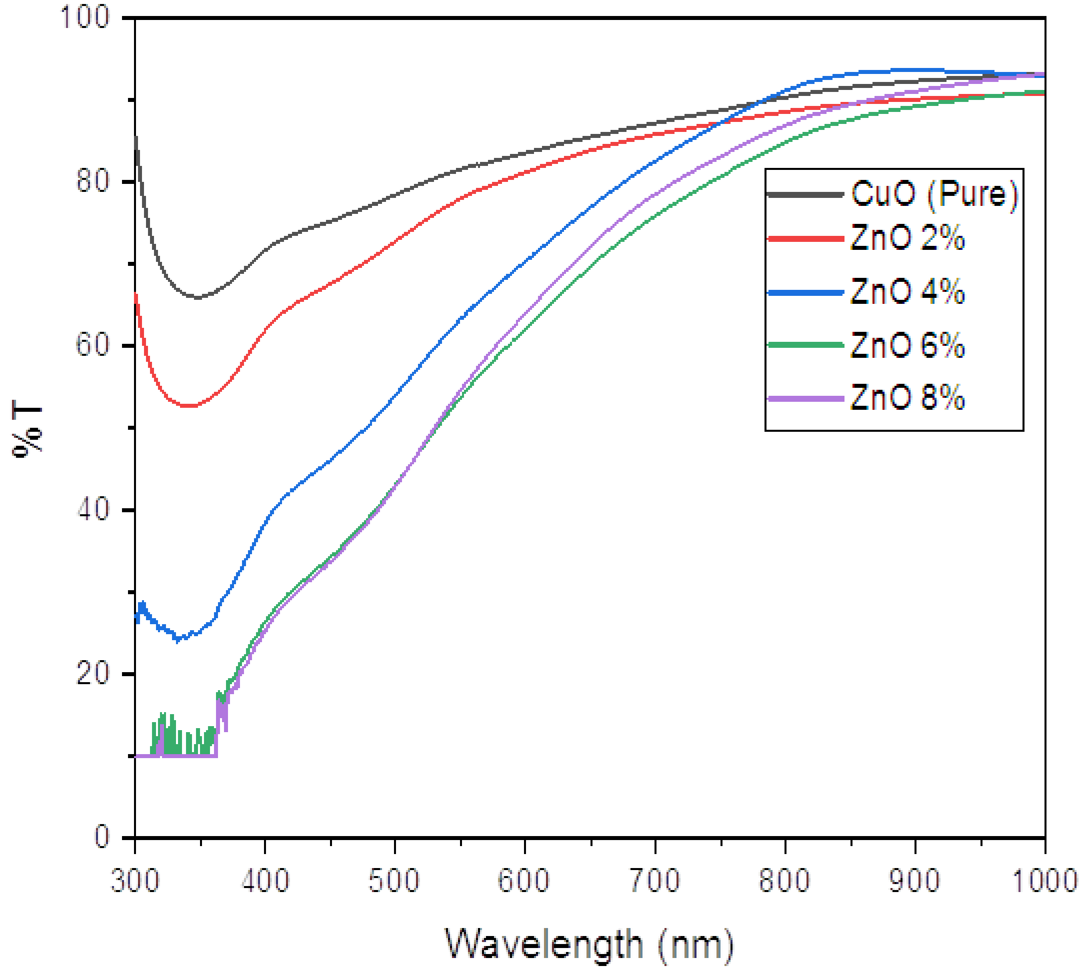

Figure 2: Transmittance spectrum of Zinc oxide doped copper oxide thin films

The spectra show a higher absorption coefficient in the wavelength of 300 nm, as shown in Figure 3, which was increased when increasing the concentration ratio from 2 to 8%. The absorption coefficient was decreased with increasing wavelength.

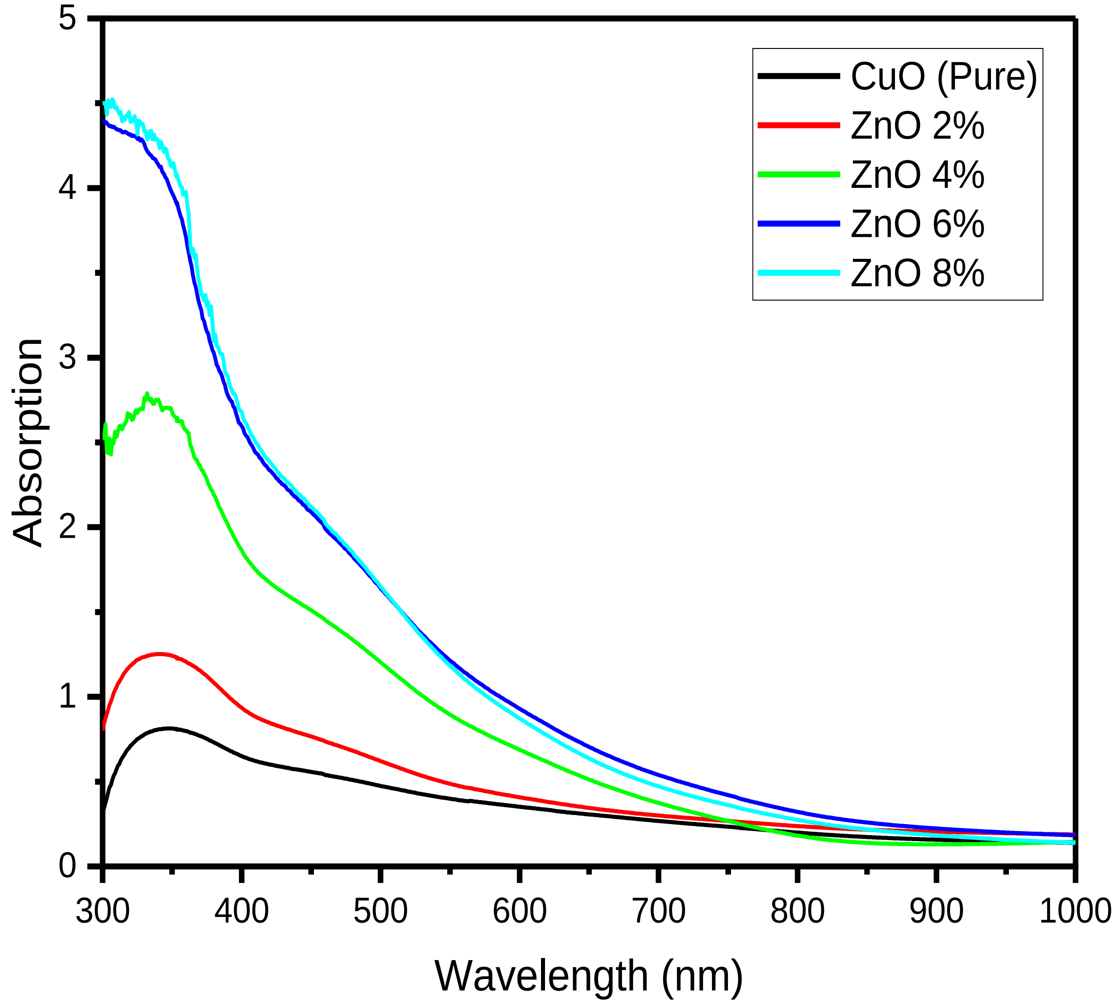

Figure 3: Absorption spectrum of Zinc oxide doped copper oxide thin films

The optical energy band gap(Eg) can be estimated by assuming a direct transition between the valence bandand conduction band using relation (2) [15,16].

The dependence of (αhυ)2 versus photon energy (hυ) for (CuO:ZnO) thin films with different dopant concentration Fig. (4). The energy gap (Eg) is estimated by extrapolating the linear part of curve (αhν)2 as a function of to intercept energy(X-axis).It was found that the(Eg)values varies from (2.589eV to 2.478eV) As shown in Table (2) with increasing (ZnO) doping concentration. reduction grain size leads to reduction grain boundaries and reduction the barrier height between the grains and finally energy gap reduction.

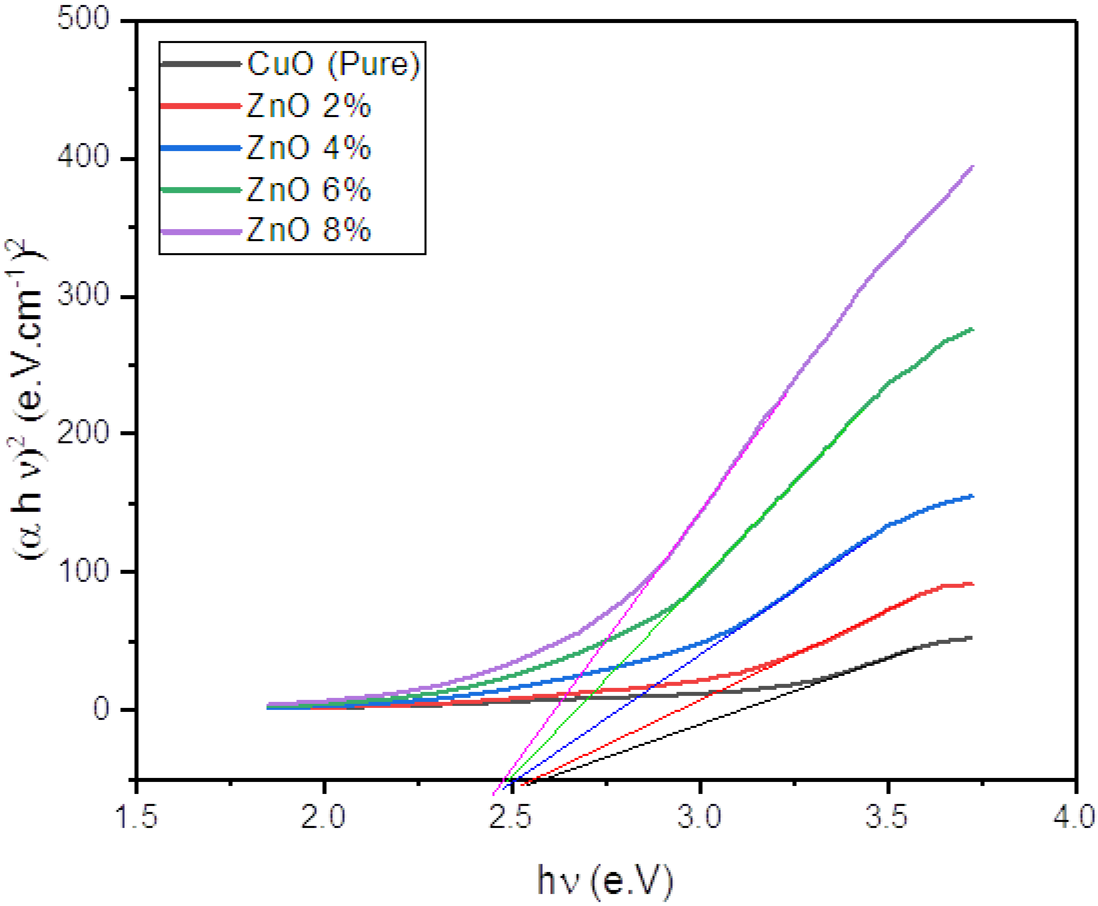

Figure 4-Optical energy gap for CuO : ZnO thin films at different ratios of ZnO

Table 2- energy gap for CuO: ZnO thin films

Sample	Eg
Pure CuO	2.589
ZnO 2%	2.561
ZnO 4%	2.516
ZnO 6%	2.502
ZnO 8%	2.478

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