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Effect of Cu doping on the Optical and Electrical properties of Thermal Spray Pyrolyzed ZnO Thin Films

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ABSTRACT:

Copper-doped ZnO (ZnO:Cu), thin films have been deposited on glass substrate at the temperature of 350ºC by TSP method at a normal environmental condition.XRD analysis shows that the studied samples belong to the (002) plane and the average grain size decrease with increasing Cu concentration. Scanning Electron Microscopy (SEM)study also shows the surface exhibits more or less uniform surface morphology with some clusters on the whole surface. The analysis of optical properties of ZnO:Cu shows good transparency with the average value of (50-75%) and also highly absorbance was measured. The value of the absorption coefficient was found to be higher order ($<10^4 cm^{-1}$) for Cu doped ZnO. Direct and indirect band gap energy were examined from 2.90eV to 3.04 eV and from 2.35eV to 2.62eV, respectively with the Cu doping concentration on ZnO. Hall effect study shows that the Cu doped ZnO films have negative hall Constant (R_H), which exhibited n-type semiconducting behavior. Although, resistivity (ρ) also decreases with increasing Cu doping concentration that's why conductivity (σ) increase swhich its semiconducting properties.

Keywords: XRD, SEM, Optical study, Hall Effect measurement, Cu doped ZnO thin film.

1. Introduction:

Now a day`s some materials are attractively used for optical devices, which has large band gap value. ZnO is one of the that type of materials, and was used as a short-wavelength light-emitting material, because it has a direct band gap of 3.37 eV at 300K compared with other materials, ZnO has larger exciton binding energy (59meV), which assures more efficient excitonic emission at higher temperatures [1,2]. Some of the main properties of ZnO are related with its optical behavior; for example, band gap reflectance and transmittance of ZnO film give some role for improving the performance of optoelectronic devices. Zinc oxide materials have non-toxicity, low cost for production and abundance in nature [3**].** These attractive properties gives priority to make this material suitable for many applications, such as solar cells, optical coatings, photo-catalysts, antibacterial activities, electrical devices, active medium in UV semiconductor lasers and in gas sensors [4,5]. Therefore, the aim of the present work was to fabricate the ZnO:Cu, thin films and to study its optical and electrical properties.

In the previous report, different research groups have studied ZnO as a research materials using various growth techniques, including RF/DC magnetron sputtering [6], chemical bath deposition [7], reactive thermal vacuum evaporation [8], pulsed laser deposition [9], sol-gel method [10]. In our experiment, we have used the low cost thermal spray pyrolysis method to prepare thin films of ZnO: Cu.

2. Measurements Procedure:

(a) Materilas:

Hydrated zinc acetate, deionized alcohol, acetic acid, zinc salt, ammonium acetate, cupric acetate

(b) Procedure for sample preparation:

In this study, we used glass substrate for the film deposition. Substrate cleaning is one of the most important factors for the fabrication of thin films. Since the optical and electrical properties of films are greatly affected by substrate surface, a good care is taken to clean the substrate surfaces. The followings steps are taken carefully for sample cleaning:

1. Firstly the glass slides were cut into desire shape. For the UV measurement, substrate dimension was about 10cm x (1~1.5) cm x (0.1)cm.
2. The slides were then immerged in water with detergent.
3. Warm it up to 1000ºC temperature for 15 minutes. Care would be taken when boiling solvents.

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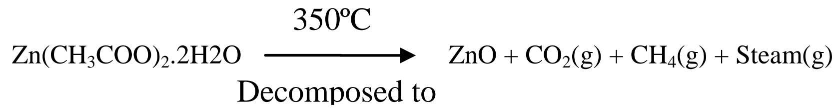
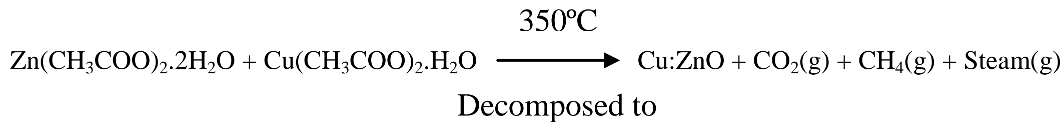
4. After cooling, substrates were again immerged in acetone and taken few minutes.

5. And finally dry it in the atmospheric environment.

(c) Solution preparation:

Pure and Cu doped ZnO thin films were deposited on glass substrate by TSP method at 350°C temperature. The detail of spray pyrolysis method is given elsewhere [12]. Three kinds of aqueous solutions such as zinc acetate, ammonium acetate and copper chloride were chosen as the source of Zn, Cu respectively. The concentration of the solutions was 0.1 mol/L. The films were produced at different atomic ratio (1,2,3 and 4 at % Cu) of ZnO. The possible chemical reactions occurred on the heated substrate to produce ZnO and Cu doped ZnO films were as follows:





3. Results and Discussion:

(a) Structural Study, XRD Analysis:

The structural properties of Cu doped ZnO films were investigated by taking X-ray diffraction (XRD) pattern. Figure 1. shows the X-ray diffraction (XRD) pattern of un-doped and Cu doped ZnO (ZnO:Cu) thin films with different Cu concentrations.The observed diffraction peaks correspond to(100), (002), and (101) planes, which confirm that all studied samples have hexagonal crystal structure which are identified by comparing with standard JCPDS card (Card no. 2100100). As can be deduced from the XRD pattern shown in Fig. 1 that the title thin films are polycrystalline in nature. These results support that, the preferential orientation of un-doped and Cu doped ZnO samples are in the (002) plane.

Determination of crystallite sizes:

The average size of crystallites was estimated by using the Debye-Scherrer formula:

$\xi = 0.94\lambda/\beta\cos\theta$………………………… (1)

Where, ξ: crystallite size, λ: wavelength of X-rays, θ: diffraction (Bragg) angle and β: full width at half maximum (FWHM) measured in radians. The calculated crystallite size or grain size for Cu doped ZnO (ZnO: Cu) films are also tabulated in Table 1.It is seen that the average grain size of Cu doped ZnO thin films reduced than that of un doped ZnO with increasing on the Cu concentration. The reduction of grain size or particle size is mainly occurred due to distortion in the host ZnO lattice because of the presence of the doped atoms. Therefore, the concentration of Zinc interstitials may be reduced due to Cu dopant concentration. This phenomenon is also well consistent with prior report [13,14]. Our results show that the average grain size along the c-axis slightly affected by Cu doping in ZnO. For 4% Cu doped ZnO sample, as an example the all peaks position has been shifted to the higher angles including of (002) plane. This shift of (002) peak might be due to the substitution of Cu atoms in the hexagonal lattice of ZnO [15].

Table-1: XRD peak positions and possible phase for Cu doped ZnO films.

Type of samples	Peak position, 2θ (deg.)	Miller Indices (hkl)	FWHM (deg.)	Grain size (nm)	Average Grain size (nm)	Lattice constants a (Å)	Lattice constants c(Å)	c/a ratio
0%Cu (Pure ZnO)	32.01 34.69 36.51	100 002 101	0.379 0.190 0.413	22.78 45.67 21.18	29.9	3.24	5.16	1.59
2% Cu (ZnO:Cu)	33.25 36.01 37.91	100 002 101	0.228 0.828 0.200	38.00 10.54 43.88	30.80	3.10	4.98	1.60
3% Cu (ZnO:Cu)	33.25 36.01 37.91	100 002 101	0.228 0.828 0.200	38.00 10.54 43.88	30.80	3.10	4.98	1.60
4% Cu (ZnO:Cu)	36.75 43.91 48.33	002 101 102	1.245 1.089 0.466	7.03 8.22 19.52	11.59	3.76	4.89	1.30

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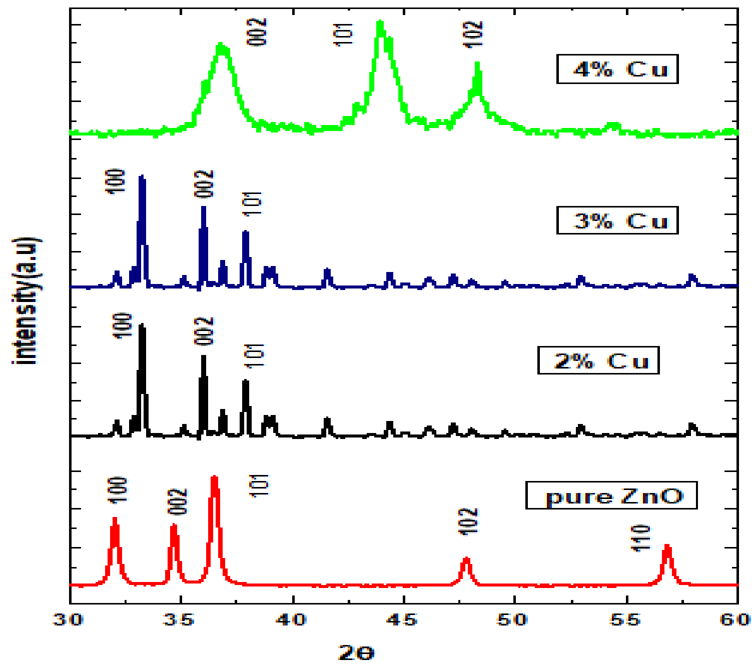

Fig. 1 (a): XRD patterns of un-doped and Cu doped ZnO thin films with different concentrations.

(b) Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) shows the surface morphology of the studied samples which are shown in Figs 2. Figure 2(a,b,c and d) show the SEM images of (1, 2, 3 and 4) % Cu doped ZnO films surfaces at low magnification respectively. It is seen that there were no strong evident of voids and cracks on the surface on the samples. The surface exhibits more or less uniform surface morphology with some clusters on the whole surface. Crystal grains are almost equal in size while a few bigger agglomerated crystal grains are distributed over the whole surface along with smaller one for Cu doped ZnO samples. These results suggested that the ZnO surface was not affected by Cu doping.

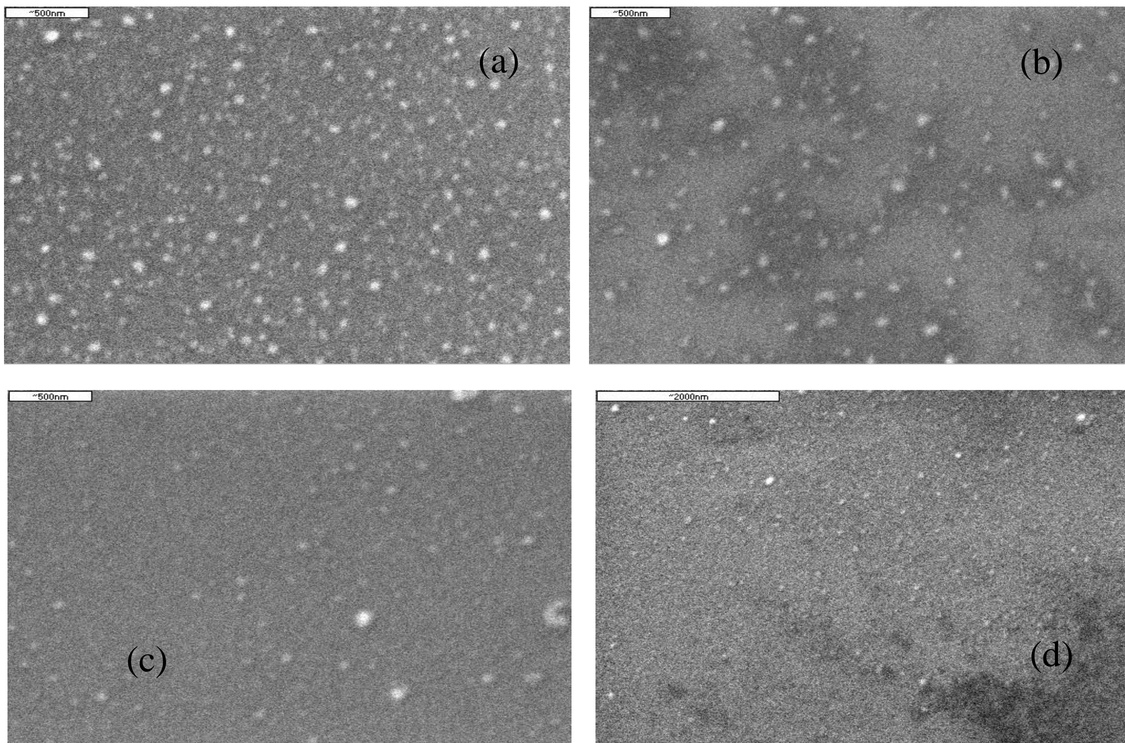

Fig. 2 (a): SEM images of 1% Cu,(b) 2% Cu, (c) 3% Cu,(d)4% Cu- doped ZnO

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4. Optical Study:

(a) Transmittance:

The optical properties of the samples are studied using UV-spectrophotometer data. Transmittance and absorption spectra for Cu-doped ZnO films were measured to investigate the optical properties of the films and are presented in Fig. 3 & 4, respectively, with the wavelength range of 380-800 nm. Here the transmittance spectra of Cu-doped ZnO films show a sharp absorption edge in the wavelength range 380-400 nm. In the visible region, the Cu-doped ZnO films shows good transparency and have an average transmittance 50% to 75% (for Cu-doped ZnO films) depending on the Cu concentration. It is noted here that the transmittance first increases sharply at the absorption edge (lower wavelength region).

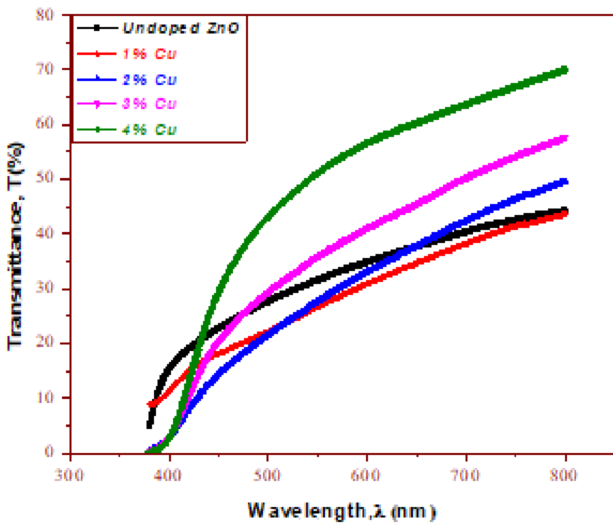

Fig. 3: Transmittance of Cu doped ZnO thin films with various concentration

(b) Absorbance:

When a light beam is impinged on a material surface, portion of the incident beam that is not reflected by the material is either absorbed or transmitted through the material [4]. Bouguer's law: The fraction of beam that is absorbed is related to the thickness of the materials and the manner in which the photons interact with the material's structure [5,6].

$$I = I_o \exp(-\alpha . x) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; (2)$$

Absorption behavior for the Cu-doped ZnO films are revealed in figure 4, with the wavelength range 380-800nm. The absorbance varies from 12-70%. Absorption is increased with decreasing the wavelength. It is gradually increase in range 800-400nm wavelength and sharply increased in 400-380nm for Cu doping ZnO thin films. On the other hand, absorption decreases with increasing in doping concentration of Cu on the ZnO thin films.

(c) Absorption co-efficient:

The value of the absorption coefficient was calculated according to the following relation [7].

$$\alpha = \frac{(2.303 \; x \; A)}{t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where t is the film thickness and A is absorbance. The variation of absorption coefficient of Cu doped ZnO films are present in figure 5. Initially the absorption coefficient increases slowly with the increasing the photon energy. But this value is rapidly increased after photon energy 3.00eV. For all films, absorption coefficient increased with increasing doping concentration of Cu on ZnO. But these values are lower the undoped ZnO. This absorption coefficient value is of the order of greater than($<10^4$ cm^{-1}) times. This behaviour indicate that this sample could be used on the solar selective surface as a good absorber.

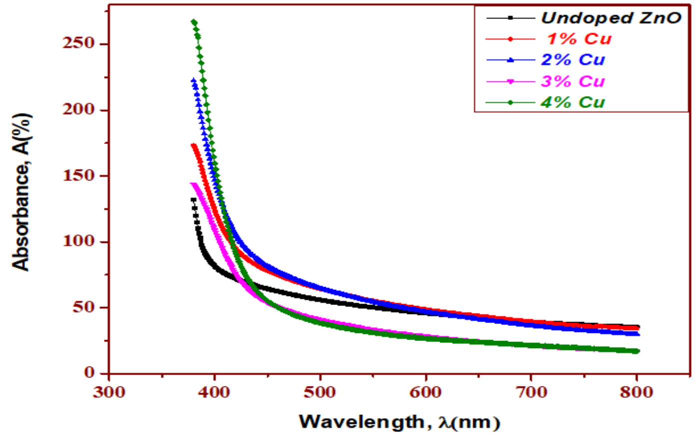

Fig. 4: Absorbance of Cu doped ZnO films with various concentration.

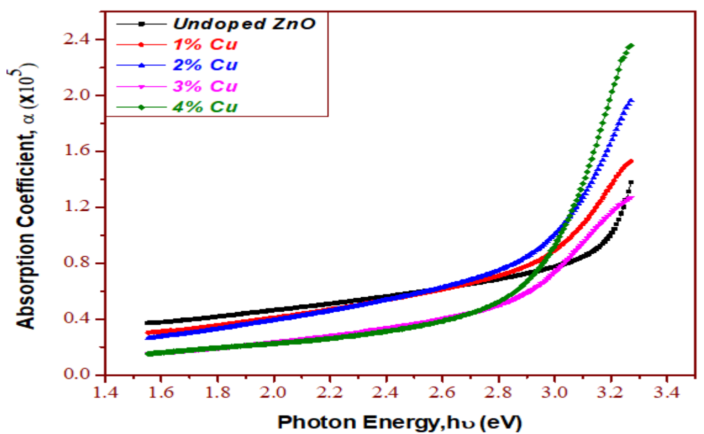

Fig. 5: Absorption coefficient of Cu doped ZnO films with various concentration.

(d) Optical Band gap:

Optical band gap of the thin films was calculated by the classical relation of near band edge optical absorption of semiconductor followed by Tauc equation:

$$(\alpha h\nu) = A\,(h\nu - E_g)^n \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where $\boldsymbol{\alpha}$ is the absorption coefficient, $\boldsymbol{h\vartheta}$ is the photon energy and $\boldsymbol{E_g}$ is the band gap energy of semiconductor and $\boldsymbol{n}$ is index related to the density of states for the energy band and determined by the nature of optical transition involved in the absorption process.

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Direct Band gap:

From the equation (4) we can calculate direct bandgap energy of these films. The direct transition involved in the absorption process, n = ½, by the plotting the value of $(\alpha h\vartheta)^2$ with the photon energy hϑ. This direct band gap of pure ZnO and Cu doped ZnO films are shown $(\alpha h\vartheta)^2$ verses photon energy (hϑ) in figure 6. The bandgap valueswere obtained by extrapolating the linear portion of the curve to intersects on horizontal ((hϑ) axis. In our investigation, the direct bandgap value of the pure ZnO was found to be 3.14 eV, although this calculated value less than the previously reported bandgap value of 3.37eV[15]. The values of the band gap energies were 2.90, 3.00, 2.88, and 3.04 eV for (1%,2%,3% and 4%) Cu doped ZnO thin films respectively. These variations of the band gap values are shown in Table 3.This results shows that,the bandgap energy increased with increasing the doping concentration of Cu on ZnO thin films. This changing of band gap with Cu doping concentration indicate that, mixd shifting occures due to the Zinc interistial atoms or oxygen vacancies which would be explained by Burstein- moss effect. We may conclude that, the band gap energy may be tuned by Cu doping on ZnO thin films. This results is also compareble with other research group [16].

Indirect Band gap

The indirect transition involved in the absorption process, n = 2, by the plotting the value of $\{(\alpha h\vartheta)\}^{(1/2)}$ with the photon energy (hϑ). The variations of indirect band gap energy of Cu doped on ZnO films are shown in figure 7. In the present investigation, the indirect bandgap of the ZnO was found to be 2.90 eV. The bandgap of the film were obtained from the intersects on horizontal axis after drawing the straight line from the curve. Observed bandgap energies were 2.35 eV, 2.49 eV, 2.31 eV and 2.62 eV, for (1%,2%,3% and 4%) Cu doped ZnO thin films respectively. In case of Cu doping, bandgap increased with increasing the doping concentration. These variations are shown in Table 3.

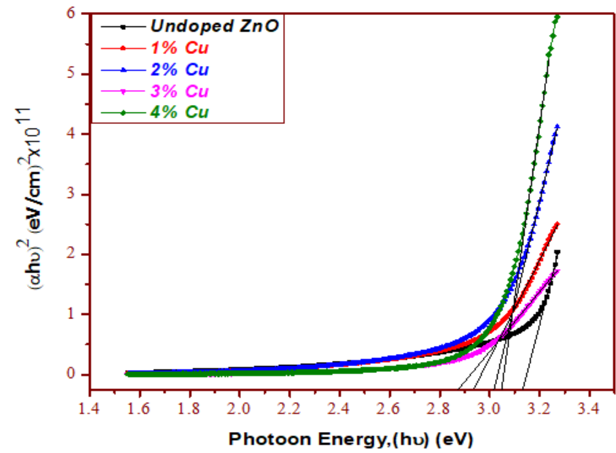

Fig. 6: Direct band gap of Cu doped ZnO films with various concentration

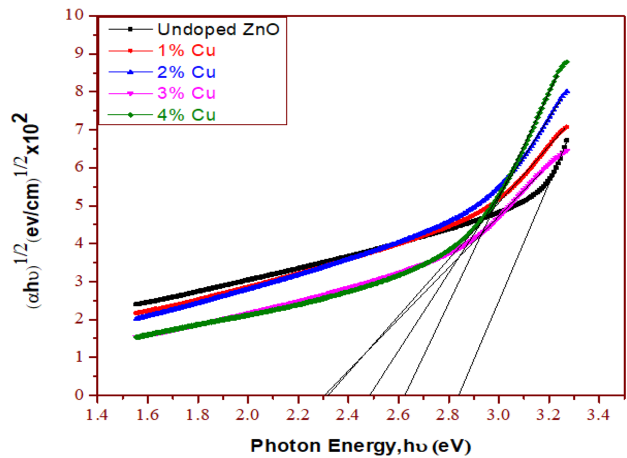

Fig. 7: Indirect band gap of Cu doped ZnO films with various concentration

Table 3: Direct and indirect band gap of Cu doped ZnO film.

Percent of Cu doped on ZnO	Direct BG of Cu doped ZnO (eV)	Indirect BG of Cu doped ZnO(eV)
0% Cu	3.14	2.90
1% Cu	2.90	2.35
2% Cu	3.00	2.49
3% Cu	2.88	2.31
4% Cu	3.04	2.62

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5. Electrical Study:

(a) Hall Effect:

Hall Effect measurement was performed to characteristics the electrical properties of the ZnO: Cu films with various Copper doping concentration. The square samples were prepared according to Van der Pau'w method with Ag paste contacts at the corners. The measurement was repeated several times to confirm the carrier types of the samples. The results indicate that ZnO: Cu films were n-type semiconductor; this goes in agreement with the previous work [15,17].

The Hall concentration (n) is related to the Hall constant (Rh) which is given below:

$$\boldsymbol{R_H} = \frac{(-1)}{qn} \qquad (5)$$

Hall mobility (μ_H) can be calculated from the relation between hall coefficient and conductivity (σ) [17].

$$\boldsymbol{\mu_H} = \frac{(\sigma)}{qn} = |\boldsymbol{R_H}|\boldsymbol{\sigma} \qquad (6)$$

Fig. 9 and Fig.10 show the variation of Hall constant (R_H), Hall mobility (μ_H), Hall concentration (n), Resistivity (ρ), and Conductivity (σ), with different Cu doping concentration. The values of Hall constant (R_H), Hall mobility (μ_H), Hall concentration (n), Resistivity (ρ), and Conductivity (σ), with different Cu doping concentration are given in Table4. It is seen that, Hall constant (R_H), and the value of Hall concentration (n), increase with increasing Cu doping concentration, on the other hand, Hall mobility (μH), finally decreases with increasing Cu doping concentration.

This phenomenon happened may be the cause of the substitution of doping Cu^{2+} creating excess new free carrier in the doping. When doping level is improving, more and more dopant atoms occupy lattice of Zn atoms which creates more charge carriers. That's way conductivity (σ), also increases [17,18]. In generally, ZnO is an n-type semiconductor, due to the presence of native defects in the form of Zn interstitial or oxygen vacancies, or may be both. A decrease in Hall mobility (μ_H) with dopant ratio may be due to decreasing grain size, indicating from our XRD calculation, which leads to increasing grain boundaries [20].

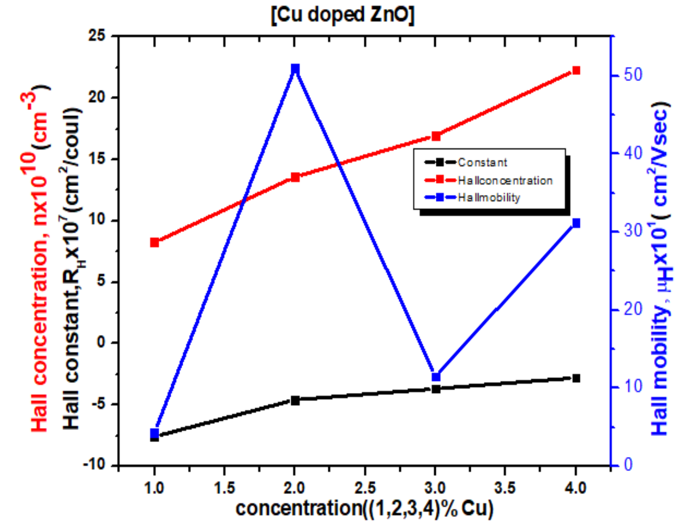

Fig. 9: Variation of Hall constant (R_H), Hall mobility (μ_H), Hall concentration (n), with different concentration Cu doped ZnO thin films.

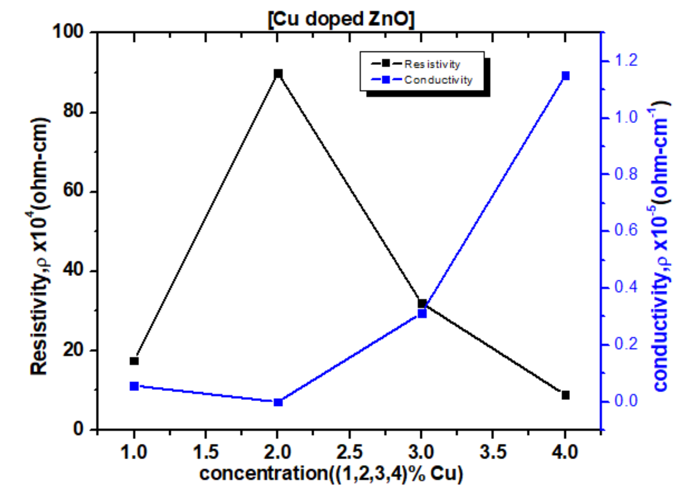

Fig. 10: Variation of Resistivity (ρ), and Conductivity (σ), with different concentration Cu doped ZnO thin films.

Table 4: Values of Hall constant (R_H), Hall mobility (μ_H), Hall concentration (n), Resistivity (ρ), and Conductivity (σ), for Cu doped ZnO.

Doping conc. (X)	Hall constant, R_H (cm^3/coul)	Hall mobility, μH (cm^2/Vsec)	Hall conc. n, (cm^{-3})	Resistivity ρ, (Ω-cm)	Conductivity σ, (Ωcm`)	Semiconductor type
1% Cu	-7.564×10^7	4.321×10^1	8.253×10^{10}	17.50×10^4	0.057×10^{-5}	n
2% Cu	-4.592×10^7	51.01×10^1	13.59×10^{10}	90.03×10^4	0.00001×10^{-5}	n
3% Cu	-3.680×10^7	11.51×10^1	16.96×10^{10}	31.99×10^4	0.312×10^{-5}	n
4% Cu	-2.798×10^7	31.20×10^1	22.31×10^{10}	8.969×10^4	1.15×10^{-5}	n

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6. Conclusions:

In this report, undoped & Cu doped ZnO films were deposited by TSP method at 350^0C. The core outcomes of the present experimental study were summarized as follows:

- XRD analysis shows the (002) plane is present for all samples. The average grain size decrease with adding Cu concentration. SEM studies confirm that, the surface exhibits more or less uniform morphology with some clusters on the whole surface.
- Optical analysis shows that the samples were good absorption coefficient($<10^4 cm^{-1}$) and bandgap energy was tuned by doping Cu on ZnO thin films.
- Hall effect study confirms that all Cu doped ZnO (Cu:ZnO) thin films have negative Hall constant (R_H), which exhibited n-type behavior. The value of Hall concentration (n), increases whereas Hall mobility (μH) decreases with increasing Cu doping concentration. That's way conductivity (σ), also increases.

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