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Structural, Electrical and Optical Characterization of Cuo Thin Films Prepared by Spray Pyrolysis Technique

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Abstract: Using the spray pyrolysis technique to prepare the P-type CuO thin films. It is carried out for three different molar concentrations of 0.10M, 0.15M and 0.20M at 350^{o} C from copper (II) chlorite precursor solution on the glass substrate. The study of X-ray diffraction attained all the films exhibit polycrystalline nature with monoclinic crystal structure comprised uniformly distributed grains. The electrical properties of the films like mobility, conductivity Hall co-efficient (R_H), and carrier concentration have been studied. Hall Effect measurement is to confirm the p-type conductivity of the films. The band gap energy size, resistivity and average particle were also determined. The resistivity has been investigated by Four probe method for different molar concentrations of copper oxide.

Key words: CuO thin films, Spray pyrolysis, Hall coefficient.

Introduction:

Different transition metal oxides (copper, iron, nickel, zinc and cobalt) have a numerous applications. One of these is cupric oxide (CuO) as an important P-type transition metal semiconductor oxide has been extensively studied. CuO has been established as a number of applications like gas sensors [1-3], solar photovoltaic [4,5], lithium ion electrode [6] etc. There are various established ways of fabricating CuO thin films like spray pyrolysis[6-9], spin coating [10,11],dip coating[12,13], SILAR[14,15] to name a few. Among all these Spray pyrolysis technique has stoichiometry in multi-component system and splendid control of chemical uniformity. As the presence of acceptor levels attributed to copper vacancies, CuO is considered to be a p-type transition metal semiconductor with a narrow band gap of 1.2 eV – 1.5 eV [15], and therefore it may be effective to construct PN junction diodes. In pure condition, the stoichiometry CuO material is an electrical insulator. However, CuO is subjected to a chemical spray, it gets deviated and thereby causes from stoichiometry due to defects and impurities.

Experimental:

In this study, the copper (II) chloride dissolving in de-ionized water to deposit CuO thin films was constructed by spray pyrolysis method. The resulting solution was mixed for 3 hours using a magnetic stirrer. The final solution, with concentration of 0.1 M, 0.15 M and 0.2 M was dark blue and clear, without any suspension of particles. The solution was sprayed onto the ultrasonically cleaned glass substrates. The substrate temperature was maintained at 350^{o}C and it was measured using thermocouple. The solution flow rate was controlled by a flow meter and kept at 2 ml min−1and the distance between the nozzle and the substrate was maintained at 15 cm. The thickness of the films was measured using gravimetric method. The crystalline structure of the copper oxide films was studied by X Pert Pro X-ray diffractometer (XRD), with CuKα radiation. The Ecopia HMS-3000 version 3.51.3 Hall effect measurement system was used to measure the Hall-coefficient, charge carrier concentration, mobility, resistivity and conductivity of the films.

Result and Discussion

Characterization by X-rays

Fig.1 shows X-ray diffraction patterns are presented for CuO thin films deposited at 350^o C for three different precursor concentrations. The obtained XRD pattern of the films for different concentration unveiled the CuO with single phase tenorite structure. The peaks at 2θ angle 35.15and 38.30, with dhkl 2.55 Å and 2.34 Å, correspond to (-111) and (111) planes respectively. (JCPDS 89-2529). From the xrd reports, increasing the precursor concentration increases the film thickness results the rise in peak intensity during the film formation. At 0.2 M concentration eight peaks at 32.12, 35.15, 38.30, 48.62, 53.18, 57.81, 65.89, and 67.75 appeared, due to (110), (-111), (111),(-202),(020), (202), (022) and (113) planes respectively. The (-111) and (111) diffraction peaks are observed for all the three samples.

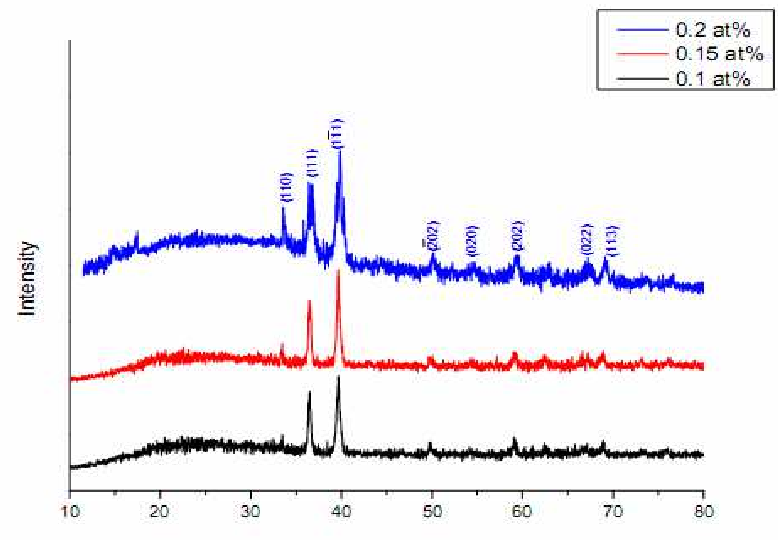

Fig.1. XRD Patterns of CuO thin film for different concentrations.

All the peaks in the XRD pattern represent the monoclinic structure of CuO. The crystallite size (D) was calculated using Scherrer's formula [16]

$$D = 0.9\lambda/\beta \cos\theta$$

where D is the crystalline size, β is the broadening of diffraction line measured at half of its maximum intensity and λ is the X ray wavelength.

From table.1 the crystalline size observed that decreasing the size with increasing the molar concentration. The optical absorption spectra was recorded in the wavelength region 300 – 1100 nm and the band gap was determined from $(h\nu)^{1/2}$ against hν graph (Fig.2) Band gap observed as 1.419 eV, 1.441 eV, 1.466 eV for the different molar concentration for 0.1 at%, 0.15 at%, 0.2 at% respectively.

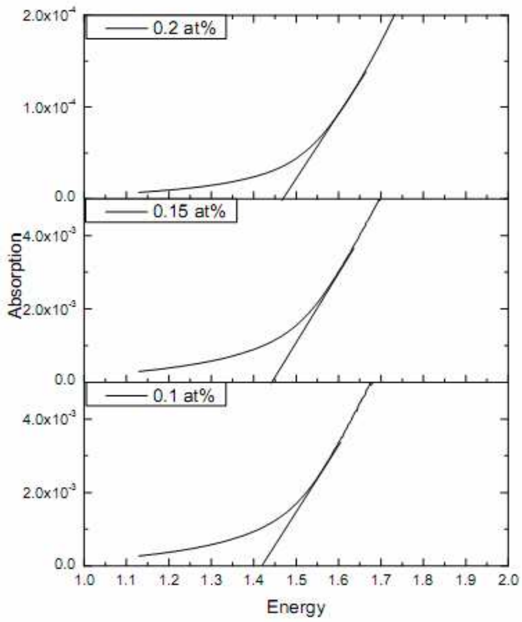

Fig. 2 Optical band gap of CuO for different concentrations

The another important optical constant, extinction co-efficient (k) has been calculated the following formula[17]

$$\mathbf{k = \alpha\lambda/4\pi}$$

Fig.3. shows that the variation of k with energy, the k value for all the films behaves a linear trend upto 2 eV after that there is a gradual decrease in the extinction coefficient value. The blue shift in the extinction coefficient value denotes that the films are stronger absorbing medium in this range.

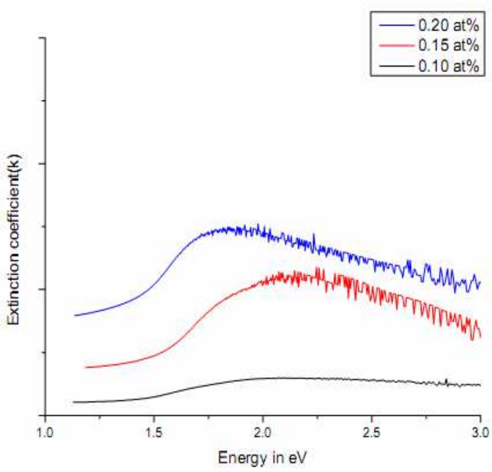

Fig. 3 Absorption co-efficient

Electrical properties

The Hall Effect measurements of the CuO thin film deposited with different molar concentration show p type conductivity and Hall coefficient increases with increasing solution concentration. The resistivity at lower concentration was first observed to be $0.18x10^4 \Omega$.cm. The molar concentration increases, the resistivity increases due to decrease in the carrier concentration.

Table.1. Electrical properties

Sample	E_g (eV)	R_H 10^7 (cm^3/C)	σ 10^{-4} ($\Omega^{-1}.cm^{-1}$)	μ 10^3 (cm^2/Vs)	ρ 10^4 (Ω.cm)	n 10^{14} (/cm^3)	D nm
0.1 at%	1.419	0.41	5.5	2.25	0.18	4.2	22.2
0.15 at%	1.441	1.40	1.54	2.16	0.65	3.6	16.7
0.2 at%	1.466	2.03	0.588	1.19	1.7	1.5	14.3

It is noteworthy to mention that the resistance value increases due to different molar concentration increases and the resistance value decreases with increasing the current for each concentration shown in Fig.4. The V-I characteristics of the deposited CuO films are shown in Fig.5. Irrespective of molar concentration, increasing the voltage the resistance value of the CuO films decreases.

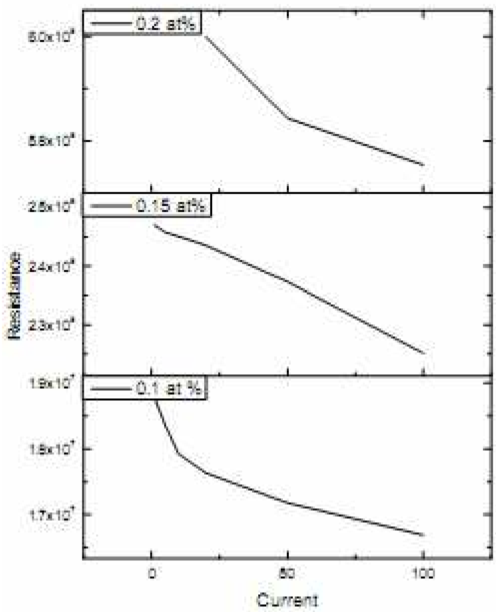

Fig.4. Current vs. Resistance.

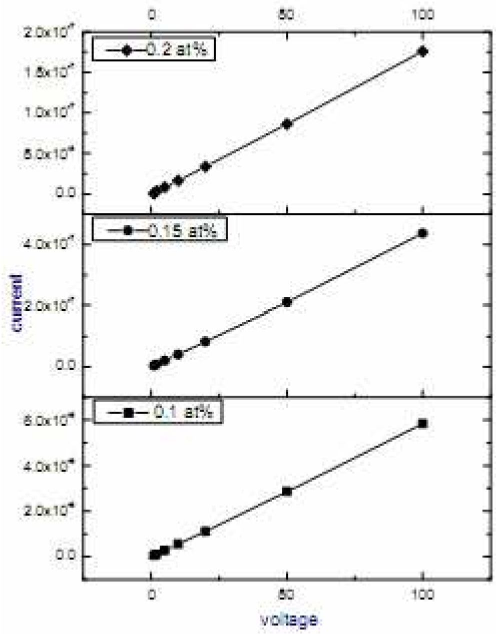

Fig.5. Voltage vs. Current

Conclusion

The consequence of variation in the precursor concentration on the optical and electrical properties was discussed for CuO films deposited at 350°C by spray pyrolysis technique. The average crystallite size was found to vary from 22 to 14 nm with increasing in concentration. The Hall Effect studies unveiled a significant decrease in mobility, conductivity and carrier concentration of CuO films for increasing concentration and it confirms that the grown films are P type in nature with the carrier concentration range of 10^{14}/cm^3. The optical absorption edges of all films were kept in the range of 350nm to 500nm.The extinction co-efficient (k) values of the grown films indicated the films are stronger absorbing medium in the lower wavelengths.

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