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Physical Properties of Copper Oxide Thin Films Prepared by Sol–Gel Spin–Coating Method

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Abstract: In this study, copper oxide thin films prepared by the sol–gel method, have been deposed onto glass substrates by the spin coating technique. Our target was to study their properties and improve them for photovoltaic use. These properties were optimized by varying the temperature annealing and the molar concentration of the precursor solutions. The effects of the annealing temperature on the structural and optical properties of the thin films are studied. It was found that the film treated at 550°C shows a higher absorbance. Then by using this optimized temperature, CuO thin films of various molar concentrations, were deposited at the same experimental conditions. The structural analysis by X- ray diffraction (XRD) shows that all the samples are polycrystalline with monoclinic crystal structure. Raman scattering measurements of all thin films confirms the structure of CuO. The optical properties of the films were characterized by UV–Visible–NIR spectrophotometry, which shows that the films show high absorbance in the visible region. Their optical band gap decreases from 3.68 to 2.44 eV when the molar concentration of precursor solutions increases from 0.1 to 0.5 M. The electrical measurements show that the resistivity of the films varies slightly from 84 Ω cm to 124 Ω cm as the molar concentration increases.

Keywords: Sol–Gel, Spin-Coating, Copper Oxide, Thin Films, Physical Properties

1. Introduction

CuO thin films have attracted much attention last years due to their electrical and optical properties [1-3]. Moreover, to lower manufacturing cost and no toxicity.

The main process to reduce the manufacturing cost is the replacement of the silicon [4] In fact, the band gap of CuO is close to that of Si [5] and GaAs [6], matching the solar spectrum more closely; therefore, the achievable solar conversion efficiency could be up to 33% for a single junction solar cell with a band gap close to 1.4eV [7, 8].

A number of reports [9-12] have been focused largely on its catalytic and gas sensitive properties; however,

photovoltaic cells based on CuO received more attention due to their excellent photovoltaic properties [13, 14] and ease of fabrication [15, 16]. Electrical and optical properties of CuO thin film depend strongly on its structure; hence, they are related to its fabricating conditions. Thus, in order to achieve higher efficiency of solar cell based on CuO thin film, it is important first to investigate their intrinsic relationship.

Copper oxide appears with 2 oxidation numbers (+1, +2), namely, cupric oxide (CuO) and cuprous oxide (Cu_2O), both of them are p-type semiconductors with optical direct band gaps at the range of 1.3 – 3.7 eV for CuO and 1.8 -2.5. eV for Cu_2O [17 - 19]. The cupric oxide possesses a direct band gap starting from 1.3 eV, which is ideal for an absorber material

to be used in solar cell applications [20, 21]. CuO thin films have been prepared using various techniques such as sol gel [22], wet-chemical synthesis [23], magnetron sputtering [24], pulsed laser deposition [17], molecular beam epitaxy [25], electro deposition [26] etc. Among these, the sol-gel is especially suitable, since it has proved to be a simple and inexpensive method, particularly useful for large area applications. This method has also the advantage that the final properties of the films can be tailored by the type and concentration of precursors as well as the annealing temperatures [27].

In this study, the fabrication and characterization of multi layer CuO films (up to four layers) on glass substrates are presented. The films were annealed in different temperatures to find the optimum annealing temperature for the excellent physical properties. By using this optimum annealing temperature, CuO thin films were prepared using different molar concentration of precursor at the starting solution. A detailed parametric study concerning the effect of annealing temperature and Cu molar concentration on the structural, optical and electrical properties of CuO thin films has been carried out. This work focuses at the amelioration of the CuO thin films properties with a view to be used as an absorbing material in photovoltaic devices.

2. Experimental Procedures

CuO thin films were prepared by the sol–gel method. First, the copper precursor solution was prepared using, copper (II) acetate [$(CH_3COO)_2 Cu/H_2O$] (98%, Sigma Aldrich), 2-methoxyethanol [$C_3H_8O_2$] (99.8%, Sigma Aldrich), and diethanolamine [$NH (CH_2CH_2OH)_2$] (MEA; 99%, Merck) as the solute, solvent, and solution stabilizer, respectively.

Copper (II) acetate was first added in 2-methoxyethanol to obtain a final concentration of 0.5 M. After 15 min of stirring at room temperature, the hot plate temperature was ramped up to 80°C and the MEA was added drop by drop and the mixture was stirred for 1 h at 80°C to obtain a transparent and homogenous solution.

Before deposition, glass substrates were successively cleaned with acetone, ethanol, and deionized water. All CuO thin films were coated onto glass substrates at a speed of 4000 rpm for 30 s and dried immediately on a hot plate at 250°C. This procedure was repeated 4 times and at the end the samples were annealed at various temperature 350, 450 and 550°C for 1 h under air. Using the same procedure samples with copper (II) acetate concentrations of 0.1 and 0.3 M in the precursor solution were prepared and annealed at 550°C for 1h under air.

The crystallographic structure of the films was studied by X-ray diffraction (XRD), using a Bruker D 8 advance, X-ray diffractometer with Cu K_α radiation ($\lambda_{CuK\alpha}$ = 1.5418Å) radiation, for 2Θ values in the range of 20–70°. The thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ±1 nm. Raman spectroscopy measurements were carried out using a Raman spectrometer (RENISHAW RAMASCOPE 2000) with a 632 nm line of HeNe laser. The optical transmittance of the films was measured by a UV-Vis-NIR spectrophotometer in the wavelength range from 300 to 1500 nm. The electrical resistivity was measured in a four point probe configuration (by a Van der Pauw method) [28]. All measurements were carried out at room temperature.

3. Results and Discussions

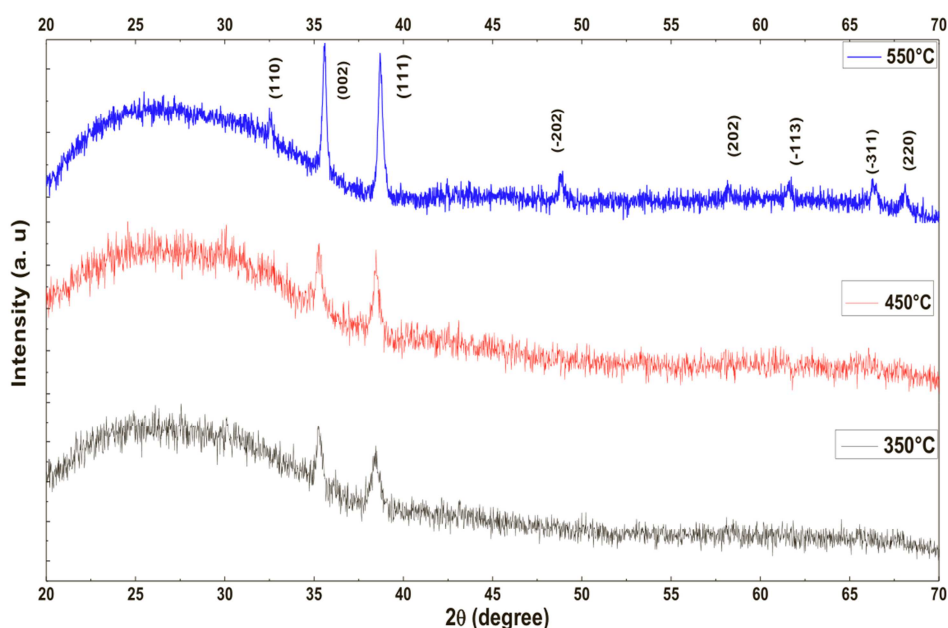### 3.1. Effect of Annealing Temperature on Physical Properties

Figure 1. X-ray diffraction patterns of CuO thin films for different annealing temperatures.

XRD analysis was carried out to investigate the structural properties of CuO thin films deposited on glass substrates and post annealing temperatures 350, 450, 550°C for 1h. Figure 1 shows XRD patterns of CuO thin films with different annealing treatment and 0.5 M Cu^{2+} initial concentration. The XRD patterns show that all annealed films have polycrystalline structures. The obtained XRD patterns of all samples matched well with the space group C2/c according to JCPDS (No. 01-089-2529) of the monoclinic CuO structure and tenorite phase. For lower annealing temperature of 350°C, the corresponding pattern shows two peaks at around 35.55 and 38.73° 2θ values, assigned to (002), (111) crystallographic plane, respectively. The intensity of these peaks is increased by increasing the annealing temperature to 450°C. For the higher annealing temperature of 550°C, a strong orientation along (002) and (111) is observed. Other peaks, such as (110), (-202), (202), (-113), (-311) and (220) are also observed, but their intensities are very small compared to the (002) and (111) peaks. From this result, it can be noted that the amorphous phase is reduced when the annealing temperature is increased. There is no significant difference between the two high intensity peaks along (002) and (111) for the different temperature. To determine the preferential orientation in CuO films, the texture coefficient was calculated from the XRD data, using the well-known formula [29]

$$T_c(hkl) = \frac{I(hkl)}{I_0(hkl)} \left[\frac{1}{n} \sum_{i=1}^{n} \frac{I(hkl)}{I_0(hkl)} \right]^{-1} \qquad (1)$$

where, I_0 (hkl) represents the intensity of reference diffraction pattern (JCPDS card no. 01-089-2529), I (hkl) is the measured intensity of the (h k l) reflection and 'n' is the number of reflections observed. The texture coefficient T_C (hkl) measures the relative degree of preferred orientation among crystal planes. Figure 2 shows T_c (hkl) values corresponding to (002) and (111) reflections for samples annealed under different temperatures. Values of $0 \leq T_C$ (h k l) ≤ 1 indicate the lack of grain oriented in the corresponding direction. As can be seen, with increasing temperature to 550°C, the texture coefficient increases slightly, indicating the increase of crystallization of (002) and (111) direction. Moreover, the Tc of (002) plane is higher than the Tc of (111) plane. It is evident that the CuO films elaborated at 550°C have the best crystallinity. These results are in accordance with the results of previous works. [30]. This improvement can be attributed to the coalescences of grains at higher annealing temperature which is confirmed by the decreasing of the full width at half maximum of peaks in the XRD patterns.

The average thickness is measured with surface profilometer and the crystallite size of the nanostructured CuO films was calculated using the Scherrer formula as follows [31]
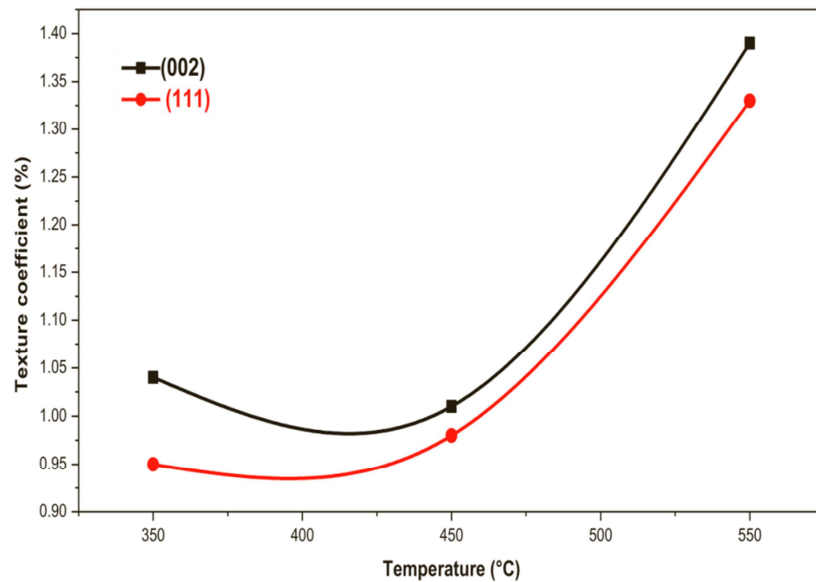
$$D = \frac{k\lambda}{\beta cos\theta} \qquad (2)$$

Figure 2. *Variation of the texture coefficient for the direction (002) and (111) as a function of annealing temperature.*

Table 1 summarizes the average thickness and the estimated average crystallite size of all samples at different annealing temperature. The crystallite size of CuO is found to increase from 16 to 32 nm, when the annealing temperature increases from 350 to 550°C. This can be explained by the merging process induced from thermal annealing [32]. The ave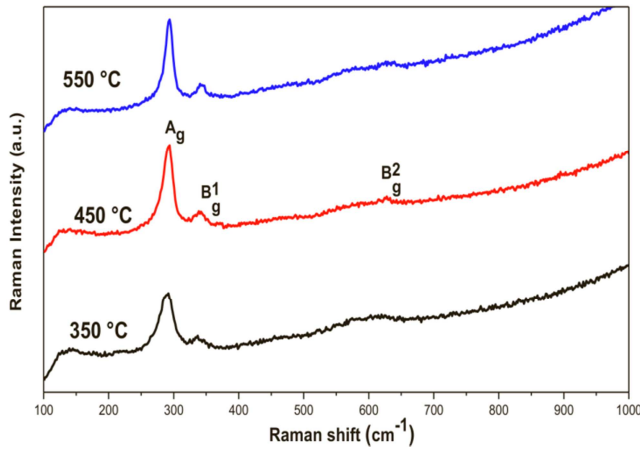rage thickness values vary from 136 nm to 252 nm. It can be seen that when the annealing temperature increase, thickness of samples also increases. This result is in accord with Ghorannevis et al [33]. It is clear from this results that the best crystallization was obtained for the 550°C annealing temperature, this result is in good agreement with Akaltun [34].

Table 1. *Values of crystallite sizes, average thickness and optical energy gap at different annealing temperatures.*

Temperature °C	Crystallite size (nm)	Average thickness (nm)	Energy gap (eV)
350	16	136	3.5
450	18	165	2.5
550	32	252	2.44

In order to complete the structural analysis of CuO thin films, Raman spectra were carried out to verify the phases present. CuO crystallizes in a monoclinic lattice with four formula units in the crystallographic primitive cell and belongs to the space group symmetry of C_{2h}^6. CuO has 12 phonon branches because there are four atoms in the primitive cell:
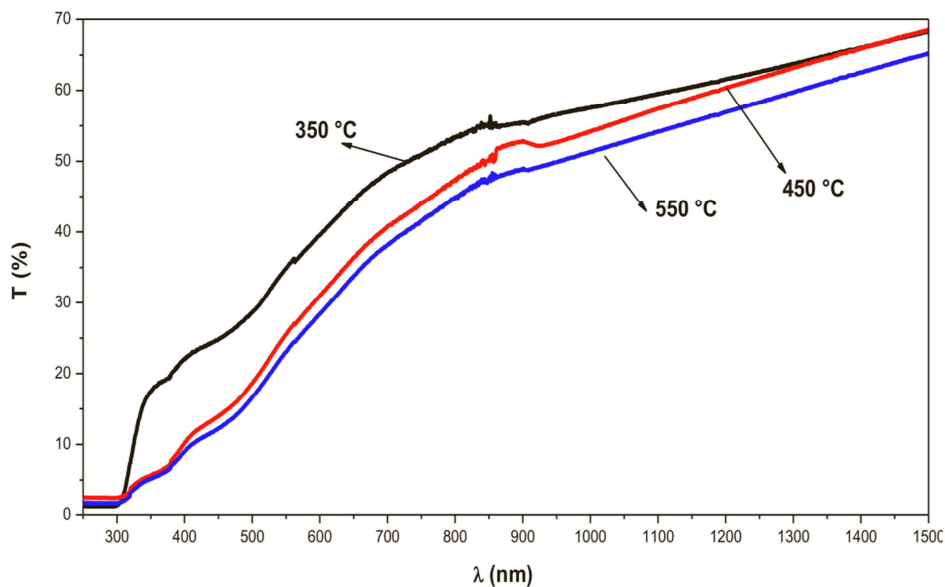
$$\Gamma_{vibr} = A_g + 2B_g + 4A_u + 5B_u \qquad (3)$$

Figure 3. *Raman spectra of CuO thin films at different annealing temperatures.*

Generally, there are three acoustic modes (Au + 2Bu), six infrared active modes (3Au + 3Bu) and three Raman active modes (Ag + 2Bg) [35]. For annealing temperatures from 350°C to 550°C, the Raman scattering revealed the presence of mixed Raman active modes. As can be seen in Figure 3, the spectrum exhibits three main phonon modes Ag and 2Bg located at 293, 339 and 624 cm^{-1}, respectively. This result confirms the presence of a single phase CuO with monoclinic structure [36].

Figure 4 shows the effect of annealing temperature in the range of 350 –550°C on the optical transmittance of CuO thin films. The film transparency decreases with increasing temperature. This behavior is due to the increase in thicknesses of CuO thin films. However, it is clear that CuO films exhibit a relatively high absorption in the visible region ranging from 400 to 800 nm, indicating suitability of the material for the solar cell applications. As can be seen, this variation is in same range reported in the literature [37, 38]. The lower IR transmittance profile of these thin films may also be due to the scattering effect of light through the optically anisotropic monoclinic structure [39]. It is observed that CuO film annealing at 550°C absorbs strongly throughout the visible spectrum with a slight transparency. The direct band gap of CuO films was determined by employing the Tauc model [40]:

$$\alpha = \frac{A(h\gamma - E_g)^{1/2}}{h\gamma} \qquad (4)$$

Figure 4. *Optical transmission spectra for CuO thin films annealed at different annealing temperatures.*

where α is the absorption coefficient of the film, $h\gamma$ is the photon energy, A is a constant and Eg the optical band gap energy.

Table 1 lists the band gap values for all samples, which show a decrease of the band gap from 3.5 to 2.44 eV with the annealing temperature, which is related to the quality of the film due to the annealing out of the structural defects [30] and

to the increase crystallites size. Our results corroborate those found in the literature [18, 41]. Dattarya et al [30] ascribed this shift in energy band gap, e.g., to the increase in crystallites size and the reduction of the amorphous phase for the annealing CuO films. In this case, the mean crystallite size increases from 15.8 nm to 32.2 nm after annealing from 350°C – 550°C. Therefore, we believed that the amorphous phase is reduced with increasing annealing temperature, since more energy is supplied for crystallite growth, thus resulting in an improvement in crystallinity of the CuO films. Moreover, it is understood that both the increase in crystallite size and the improvement of the crystallinity are responsible for the band gap decreasing with increase annealing temperature of CuO films. The annealing temperature of 550°C seems to be the best, with best properties studied. Based on the obtained results, the annealing temperature was fixed to 550°C.

3.2. Influence of the Precursor Molar Concentration on Copper Oxide Thin Films

3.2.1. Structural Characterization

Figure 5 shows the X-ray diffraction patterns of CuO thin films with different molar concentrations, 0.1, 0.3 and 0.5 M. The X-ray diffraction patterns of CuO thin films elaborated with 0.1M show high intensity of picks observed at $2\theta = 35.55°$ and $38.73°$ corresponds to the (002) and (111) diffraction planes and some small peaks assigned to (110), (-202), (202), (-113), (-311) and (220) observed at $2\theta = 32.52$, 48.74, 58.30, 61.56, 66.25 and 68.13°, respectively. It can be noticed that the XRD pattern has not much altered by increasing in molar concentration. All the apparent atomic plans revel that the deposited films are composed of a single CuO phase with monoclinic crystal structure. Based on these results from the present study, the sol–gel method combined with the spin–coating technique and optimized deposition parameters yield to only the single tenorite CuO phase with monoclinic structure at the higher annealing temperature of 550°C. The (002) and (111) diffraction peaks of CuO was intensified in the process of increasing the concentration due to the increase in thickness of the film, which is consistent with the results reported by R. Shabu et al. [38].
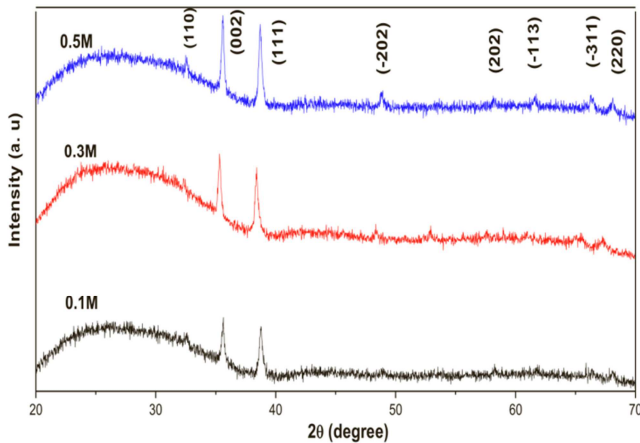
Figure 5. *X-ray diffraction pattern CuO thin film with different precursor molar concentration.*

The different texture coefficients T_C (hkl) have been calculated from the X-ray data. We have calculated the texture coefficient for the two dominated atomic plan (002) and (111). The T_C (hkl) values for 0.3 M are lower than 0.1 M and the 0.5 M are higher than both as shown in Figure 6. In all the cases, the T_c of (002) plane is slightly higher than that of (111) plane.

All films have a polycrystalline nature and the calculated texture coefficient shows that the CuO films elaborated with precursor concentration equal to 0.5 M have the best crystallinity.
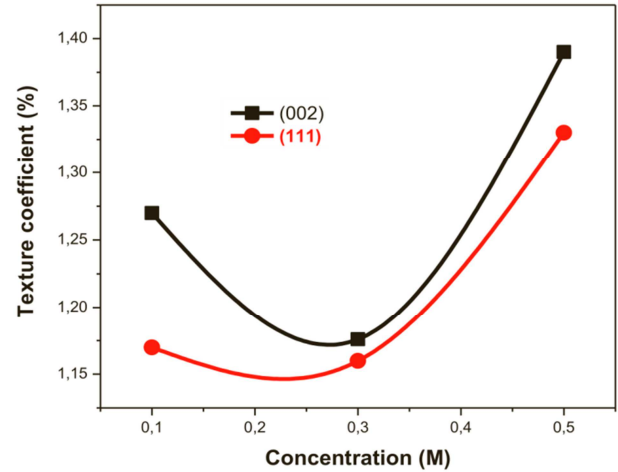
Figure 6. *Variation of the texture coefficient for the direction (002) and (111) as a function of precursor molar concentration.*

The variations of crystallite size and strain with molar concentration are shown in Figure 7. The average crystallite size deduced from the full width at half the maximum (FWHM) of (200) planes was estimated using Scherrer's relation [29]. The strain (ε) developed in films due to lattice misfit was evaluated using Eqs [42].

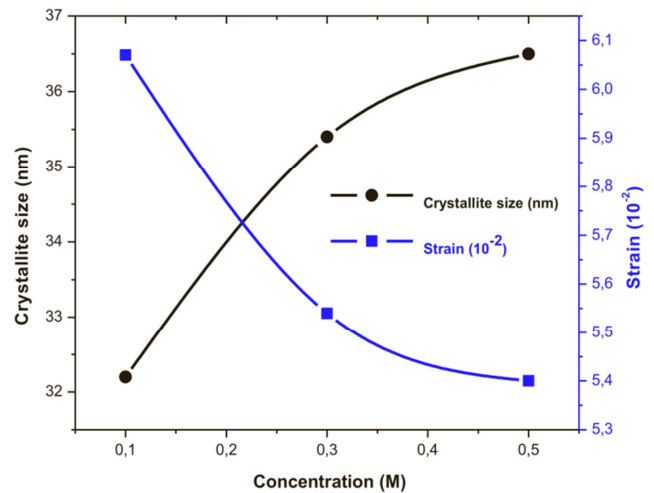$$\varepsilon = \frac{\beta cos\theta}{4} \tag{5}$$

Figure 7. *Crystallite size and strain of Cu-oxide thin films as a function of precursor molar concentration.*

It is apparent from the figure that crystallites size increase

with increasing the molar concentration. This variation can be related to the increase in film thicknesses. In addition, the increase in the precursors molarity leads to increase in Cu concentration which results in a higher condensation of Cu atoms and faster nucleation in consequence a growth of bigger crystallites. On the other hand, strain decrease with increasing the precursors molarity. From these results, it was confirmed that the fundamental effect of increase in crystallite size is related to decrease in strain. The decrease in strain indicates the decrease in lattice imperfections, formation of high quality films and better crystallization of high quality CuO thin films. Furthermore, this can make CuO films, very interesting for photovoltaic applications [38].

3.2.2. Optical Properties

The optical transmittance spectra, recorded in the wavelength range from 300 nm to 1800 nm of copper oxide thin films prepared using different molar concentrations are shown in Figure 8. The films prepared from 0.1 M showed a maximum transparency of 88% in the visible region. The spectra demonstrated a decreasing transparency from 88% to 60% by increasing the concentration from 0.1 to 0.5 M. Consequently, the decrease in optical transmittance with the increase in copper concentration can be attributed to the increase in films thicknesses. The average thickness of the obtained samples with different Cu concentration is presented in Table 2. It was observed that the average thickness increases with molar concentration from 133 to 253 nm as it is expected due to the increased quantity of Cu acetate used. For films with 0.3 M and 0.5 M, the spectrum shows relatively high absorption in the region (300 – 800 nm) and lower absorbance in the NIR and IR regions.
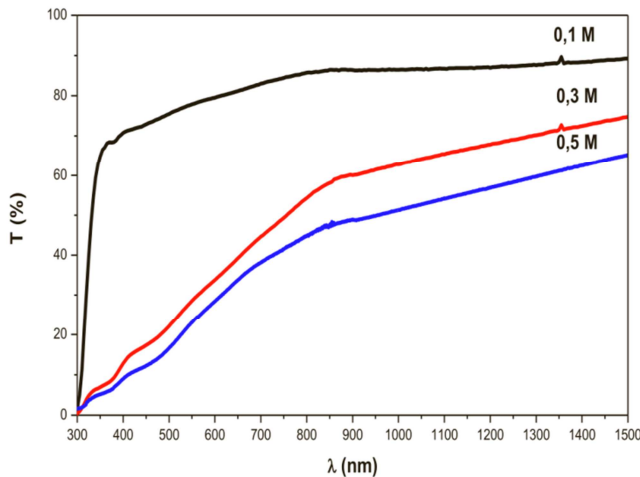

Figure 8. *Transmittance spectra of thin films deposited using 0.1, 0.3 and 0. 5 M precursor molar concentration.*

Table 2. *Values of average thickness and optical energy gap for various Cu molar concentration.*

Cu molar concentration (M)	Average thickness (nm)	Energy gap (eV)
0.1	132	3.68
0.3	175	2.56
0.5	252	2.44

The direct band gap of CuO films was determined from Tauc relation. The obtained results are presented in Table 2. It was found that the band gap decreased from 3.68 to 2.44 eV with increase molar concentrations of CuO thin films. The CuO samples elaborated with 0.1M show higher direct band gap (3.68 eV), reported by [3], as compared to bulk value (1.3 eV – 2.1 eV) [2]. The decrease in band-gap may be attributed to the increase in films thicknesses of Copper oxide [43].

Therefore, it is clear for the sample elaborated with 0.5 M, a strong absorption observed at lower wavelengths and low band gap energy is obtained (about 2.44 eV). Hence these films have potential for the application of the films as absorber layer in solar cell fabrication [44].

3.2.3. Electrical Properties

The electrical resistivity was measured by the Van der Pauw method [28] in four-point configuration its dependence with the molar concentration is shown in Figure 9. The resistivity value increases slightly from 84 Ω cm to 124 Ω cm with the molar concentration. The raise of the crystallite size leads to an increase in the grain boundaries density. The increase of the electrical resistivity with the increase of crystallite size indicates that the conduction mechanism is driven by grain boundary scattering. Similar results, in the range 37.83 - 119.24 Ω cm, are reported by K. S. Wanjala et al. [44].
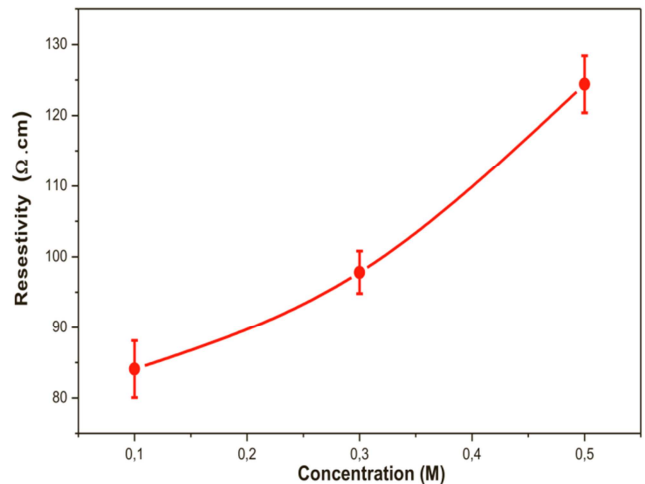

Figure 9. *Electrical resistivity for CuO thin films as a function of different precursor molar concentration.*

4. Conclusions

We have studied the effect of both annealing temperature and molar concentration on physical properties of CuO thin films deposited on glass substrates by a sol-gel spin–coating method. The best crystallinity and higher absorbance were found for films annealed at 550°C. The optical band gap of CuO thin films decrease to 2.44 eV after annealing at 550°C. From the investigation of molar concentration, XRD analysis indicates that all deposited film are polycrystalline in nature with monoclinic structure The decrease in optical transmittance with

the increase of molar concentration was attributed to the increase of the film thicknesses. We can notice that CuO film exhibit high absorption in the visible spectrum. This behaviour is very interesting for the use of CuO as an absorber layers in solar cells. The electrical resistivity increases with molar concentration, ranging between 84 Ω cm to 124 Ω cm.

These results show that CuO films prepared by sol–gel spin–coating method can be used for preparation of solar cells [38, 43]. These films can be prepared at relative low temperatures of 550°C showing good crystallinity with preferred orientation at (002) and (111) diffraction planes. Moreover we can start from relative high concentrations (0.5 M) to achieve thicker films with better properties. We intend to proceed by doping the CuO films with metals, to obtain films with lower resistivity.

Acknowledgements

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