Effect of annealing temperature on structural and optical properties of copper oxide thin films deposited by sol-gel spin coating method

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In this study, CuO thin films synthesized via simple sol-gel method, have been deposited on glass substrates by the spin coating technique and annealed at various temperatures. Samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier-transform infrared (FT-IR) and Raman spectroscopy, and UV-visible spectroscopy. The structural characterization by XRD reveals that the as prepared films were tenorite phase and have a high level of purity and crystallinity. The crystallite size of the CuO films was affected by the annealing temperature and was estimated in the range 20-31.5 nm. SEM images show a homogeneous distribution of spherical nanoparticles over the surface of the annealed films at 350 and 450 °C. Vibrational Spectroscopy revealed vibration modes specific to CuO with monolithic structure on the Raman spectra at 289 cm^{-1} and on FT-IR spectra around 430-580 cm^{-1}.Electronic investigation performed by UV–Visible spectroscopy showed that the films have high absorbance in the visible region and their optical band gap increases from 2.40 to 2.66 eV (blue shift) with increasing annealing temperature from 350 to 550 °C.

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1. Introduction

Copper oxide in the form of thin films is often used as an active layer in solar cell applications [1]. It is a p-type semiconductor with two possible phases: cupric oxide or tenorite oxide (CuO) and cuprous or cuprite oxide (Cu_2O) of monoclinic and cubic structures with band gap values of 1.3-2.1 eV and 2.0-2.6 eV respectively [2]. Copper oxide has received a great deal of attention because of its non-toxicity, low cost, and high solar absorbance; these properties make it a cost-effective and promising nanomaterial device for applications such as batteries, gas sensors, photovoltaic cells [3], field emitters and photocatalytic reactions [4]. During the last decades, many ways have been used for the synthesis of thin layers of copper oxide, such as spin coating and dip coating sol-gel[5], electrodeposition [6], spray pyrolysis technique [7], thermal oxidation [8], and plasma evaporation [9].

In this study, we used the sol-gel spin coating method to synthesize the thin films of copper oxide deposited on glass substrates. The use of the sol-gel technique has many advantages, including excellent control of chemical homogeneity and stoichemic precursors, easy incorporation of a wide range of functional groups, comparatively low annealing time, control of nanoparticle size and crystallization at low temperature, simple and economical treatment for the equipment. The objective of this work is to prepare thin films of copper oxide and to study the effects of an annealing temperature ranging from 350 to 550°C on its structural, morphological and optical properties.

2. Experimental

Copper oxide thin films were deposited on glass substrates by the sol–gel method using the spincoating method. First of all, the glass substrates were cleaned in hydrochloricacid (HCl), acetone and rinsed with distilled water, and sonicated with ultrasonic cleaner consecutively. Two primary solutions have been prepared; the first solution by dissolution of 2gof copper (II) chloride anhydrous ($CuCl_2$) (98%, Biochem) in 10 ml of methanol (CH_3OH), with constant magnetic stirring. When a transparent solution is obtained, 185 µl of glycerol ($C_3H_8O_3$) are added thereto. The second solution is obtained by dissolution of 870 µl of trimethylamine (C_3H_9N) in 10 ml of methanol; then 1 µl of HCl is added to facilitate the dissolution of the solution, followed by a few drops of distilled water. Storing the mixture of the two previous solutions for 24 hours at room temperature gives a resulting solution completely yellow-green.

All CuO thin films were coated on glass substrates at a speed of 2800 rpm for 40 s and dried immediately on a hot plate at 100°C for 10 minutes. This procedure is repeated three times (three layers) and at the end, the samples were annealed at the temperatures 350, 450 and 550°C for 1 hour in air.

The crystallographic structure of the films was studied by X-ray diffraction (XRD) in the 2θ range 20–80°, using a Bruker D8 advance X-ray diffractometer with CuK_α radiation ($\lambda_{CuK\alpha}$=1.5418 Å). The morphology was analyzed using scanning electron microscope (SEM) JEOL JSM-6360LV. Raman spectroscopy measurements were carried out using a Raman spectrometer (LabRAM HR Horiba JobinYvon) with a 633 nm line of He-Ne laser. The optical absorption of the films was measured by a UV-Vis-NIR spectrophotometer (Shimadzu, UV-3101 PC) in the wavelength range 300-800 nm. All measurements were carried out at room temperature.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction patterns of the copper oxide thin films annealed in air at different temperatures ranging from 350 to 550 °C are shown in Fig. 1.

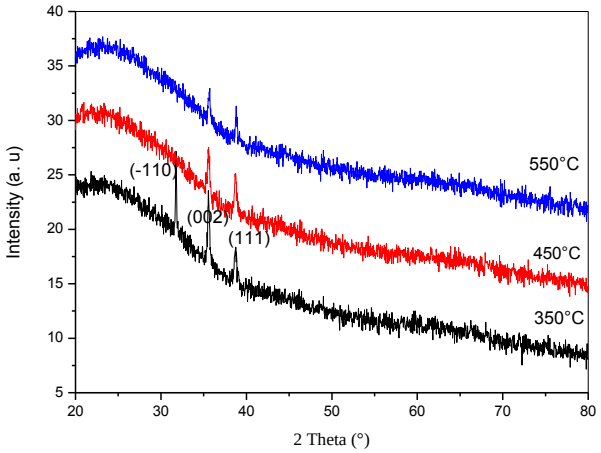

Fig.1. X-ray diffraction patterns of CuO thin films for different annealing temperatures

The presence of peaks indicates that all the annealed films are polycrystalline. For the sample annealed at 350 °C, three well defined diffraction peaks are observed at the 2θ angular positions 31.85°, 35.60° and 38.81°. They can be assigned to reflections from $(\bar{1}10)$, (002) and (111) crystallographic planes of monoclinic structure of CuO (tenorite phase) with lattice parameters: a = 4,685 Å, b = 3,425 Å, c = 5,130 Å, β = 99,54° and space group C2/c according to the JCPDS card N° 00-045-0937. The CuO thin films have mainly (002) and (111) crystalline orientations. The intensity of the peaks reflects the good crystallization of the CuO particles; this result is in good agreement with those recently reported by M. Dahrul et al. [10].Moreover, for the annealed samples at 450 and 550 °C, the disappearance of the peak at the 31.85° position could be due to a recrystallization of this peak in favor of the other peaks. The average crystallite size of the nanostructured CuO thin films was calculated using Debye-Scherrer formula [11]:

$$D = \frac{0{,}9\lambda}{\beta \cos\theta} \quad (1)$$

where D is the crystallite size, λ is the wavelength of the incident ray, β is the Full Width at Half Maximum value (FWHM) of the diffraction line and θ is the Bragg diffraction angle. Table 1 summarizes the estimated average crystallite size of all samples at different annealing temperatures. The (111) plane was used as a reference to calculate the crystallite size for the copper oxide thin film. The crystalline size increases from 19.99 to 31.47 nm for temperatures from 350 to 550 °C. This can be explained by the merging process induced from thermal annealing [12].

Table1. Values of crystallites size of (111) plan at different annealing temperatures

Temperature (°C)	2θ (°)	FWHM (°)	Crystallites size (nm)
350	38.81	0.44049	19.99
450	38.81	0.32535	27.06
550	38.81	0.27978	31.47

3.2. Raman analysis

Raman spectrometry is an important tool to analysis the phase of the material prepared. CuO has 12 phonon branches because there are four atoms in the primitive cell, three acoustic modes ($A_u + 2B_u$), six infrared active modes ($3A_u + 3B_u$) and three Raman active modes ($A_g + 2B_g$) [13]. It is well known that pure CuO nanoparticles possess bands at A_g (296 cm^{-1}), $B_g(1)$ (346 cm^{-1}), $B_g(2)$ (631 cm^{-1}) [14]. For annealing temperatures from 350°C to 550°C, the Raman scattering revealed the presence of Raman active mode. As can be seen in figure 2, the spectrum exhibits the main phonon mode A_g located at 289 cm^{-1}. This result confirms the presence of a single phase CuO with monoclinic structure [15].

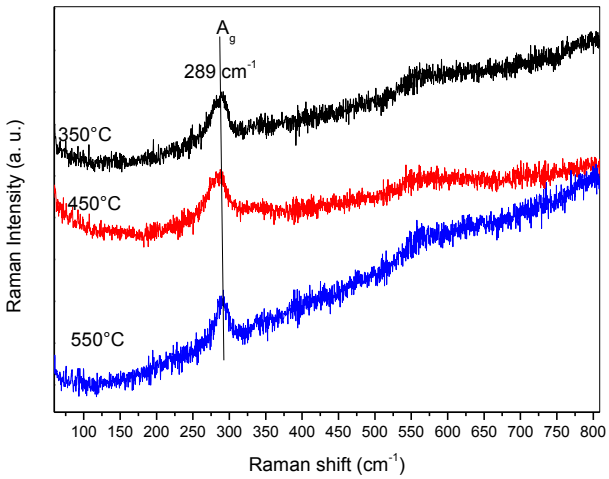

Fig.2. Raman spectra of CuO thin films at different annealing temperatures

3.3. FT-IR analysis

The FT-IR spectra of the CuO thin films recorded in the range 1400-359 cm^{-1} are shown in figure 3. A broad transmittance band of metal-oxygen bond was found around 430–580 cm^{-1} [16] which was assigned to vibration of the Cu-O bonds, thus determining the presence of CuO in the system. The band at around 480 cm^{-1}, is common between the three spectra which can be assigned to the vibrations of Cu(II)-O bonds. We also note the emergence of a band at around 500 cm^{-1}in annealed films at 550 °C assigned to the vibrations of Cu(II)-O bonds[17].

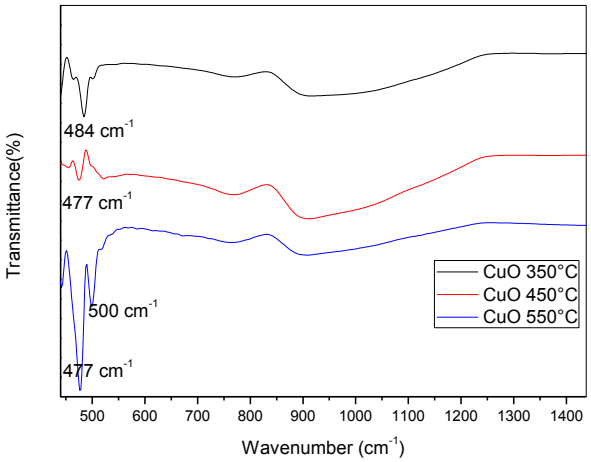

Fig.3. FTIR spectra of CuO thin films at different Annealing temperatures

3.4. Morphological analysis

The surface morphology of the prepared CuO thin films was revealed through the SEM images shown in figure 4. It shows a homogeneous distribution of spherical shape of the prepared CuO nanoparticles. On comparison of the three micrographs it could be observed that the surface morphology of the samples at 350°C and 450°C exhibited uniform and relatively dense surface with a small crystallite size (lower than 100 nm). Moreover, the surface morphology of the sample at 550°C shows a cloud-like structure.

We found that the particle size distribution depends on the annealing temperature and that its growth mechanism is a nucleation process that began when Cu^{2+}reacted with $O^{2-}$from the air to form CuO molecules, which are uniformly distributed then immediately agglomerated. The increase in particle size with annealing temperature was likely caused by removal of traces of carbon on the surface of the particles, which forced neighboring particles to agglomerate and create eventually larger particles [18]. The average particle sizes derived from SEM images are slightly greater than the results of the XRD profile shown in Table 1.

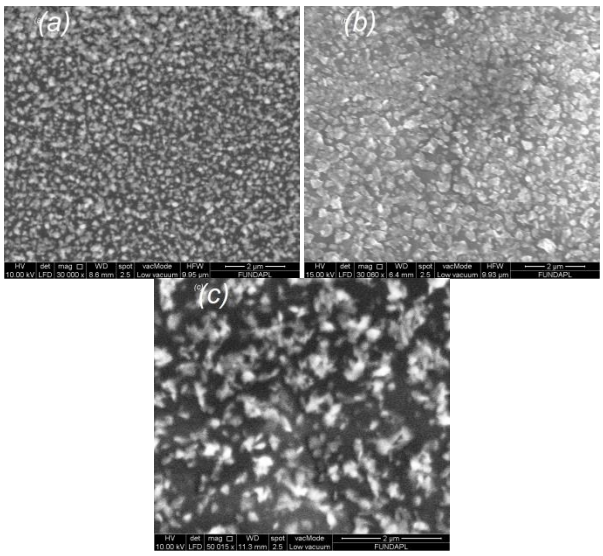

Fig.4. SEM image of CuO thin films at different annealing Temperatures: a)350 °C, b)450°C, c)550°C.

3.5. Optical analysis

Fig. 5 shows the effect of annealing temperature on the optical absorption of CuO thin films. 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, especially the annealed films at 450 ° C. The direct band gap of CuO films was determined by employing the Tauc model [19]:

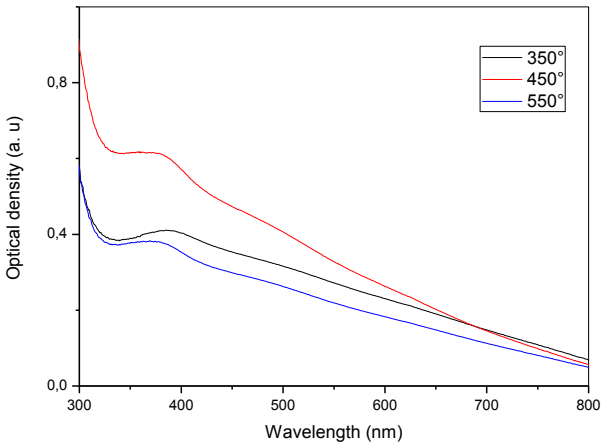

Fig.5. Optical absorption spectra for CuO thin films at differentannealing temperatures.

$$\alpha h\upsilon = C(h\upsilon - E_g)^{1/2} \qquad (2)$$

where α is the optical absorption coefficient, hυ is the photon energy, $E_g$is the optical band gap and C is the constant for a direct transition. The values of $(\alpha h\upsilon)^2$ versus (hυ) plotted for annealed samples at 350, 450 and

550°C are shown in Fig. 6. Straight lines fitting the linear part of experimental curves were drawn and elongated to cut off the energy axis (hυ) to define the optical band gap values E_g. We found the following optical gap values 2.40, 2.55 and 2.66 eV for annealed films at 350, 450 and 550 °C respectively. Thus, the band gap increased with increasing annealing temperature, as compared to bulk value 1.3–2.1 eV [2]. The increase in band gap (blue shift) may be attributed to the quantum confinement effect [20].

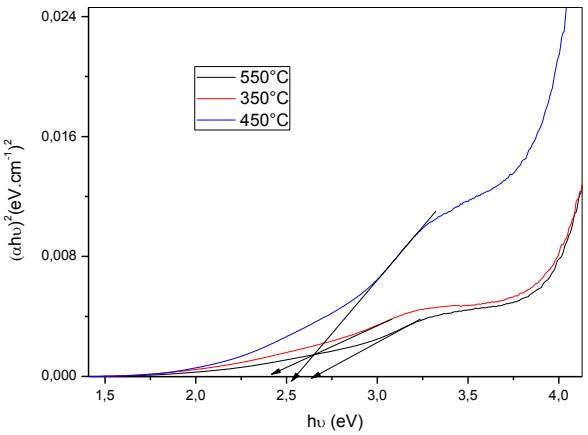

Fig.6. Band gap energy for CuO thin films at different annealing temperatures.

4. Conclusion

In this work copper oxide thin films have been successfully synthesized by sol gel method and deposited on glass substrates by spin coating technique and annealed at various temperatures. The structural, morphological, vibrational and optical properties of the samples were studied. The XRD analysis reveals that CuO thin films were tenorite phase and that the best crystallinity is found for annealed films at 350°C. Raman spectroscopy confirms the presence of a single phase CuO with monoclinic structure. SEM images show that the surface morphology of the films was affected by the annealing temperature. The optical band gap of CuO thin films increased from 2.40 to 2.66 eV with increasing annealing temperature. The annealed CuO films at 450°C exhibit a relatively high absorption in the visible region, indicating suitability of the material for solar cell applications.

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