

Annealing Effects on the Properties of Copper Oxide Thin Films Prepared by Chemical Deposition

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Copper oxide thin films with thickness of 0.45 μm were chemically deposited on glass substrates by dipping the microscope glass slide for 20 s each in 1 M NaOH and copper complex solutions. Temperature of NaOH solution was increased to 70 $^{\circ}\text{C}$, while the copper solution was maintained at room temperature. Copper oxide thin films were annealed in air at different temperature of 200 - 400 $^{\circ}\text{C}$ and as-prepared sample was used as reference. The films structures were studied by XRD. The patterns showed that the films as prepared and annealed at 200 $^{\circ}\text{C}$ were cuprite structure with Cu_2O composition. Films annealed at 300 $^{\circ}\text{C}$ consist of mixed tenorite (CuO) and cuprite (Cu_2O) phases. Annealing the films in air at 400 $^{\circ}\text{C}$ completely converts these films to tenorite structure with composition of CuO . The proportion of the two forms of copper oxide varies with oxidation temperature. The surface properties were characterized using scanning electron microscopy. UV-Vis transmittance spectra confirmed the results from the XRD by a shift in the optical band gap from 2.40 to 1.73 eV. The conversion was also confirmed by the FTIR spectroscopy measurement. Photoluminescence intensity is greatly improved with the increase in annealing temperatures.

Keywords: Annealing; Deposition; Optical Property; Thin Film

1. INTRODUCTION

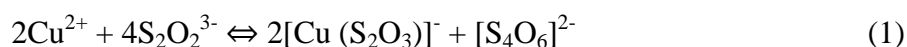
Copper oxides are semiconductors that have been studied for several reasons such as the natural abundance of starting material copper (Cu); the easiness of production by Cu oxidation; their non-toxic nature and the reasonably good electrical and optical properties by Cu_2O [1]. Copper forms two well-known oxides: tenorite (CuO) and cuprite (Cu_2O). Both the tenorite and cuprite were p-type semiconductors having band gap energy of 1.21 to 1.51 eV and 2.10 to 2.60 eV respectively [2,3]. As a p-type semiconductor, conduction arises from the presence of holes in the valence band (VB) due to

doping/annealing [4]. CuO is attractive as a selective solar absorber since it has high solar absorbency and a low thermal emittance [5]. Cu₂O is very promising candidate for solar cell applications as it is a suitable material for photovoltaic energy conversion [6-8]. Polycrystalline thin and thick films of copper oxide have been prepared by various techniques such as thermal oxidation, electro deposition, chemical conversion, chemical brightening, spraying, chemical vapor deposition, plasma evaporation, reactive sputtering and molecular beam epitaxy [9-11]. Ristov *et al* [9] reported a chemical deposition method for Cu₂O thin films on glass substrates. The method consists of alternate immersions of the substrates in solutions of hot NaOH and in a complex of copper ions repeated over 5 – 40 immersion cycles. Lower preparation costs, the significant of higher coating speed and purity, convenient for large area deposition and a wide flexibility in the choice of the chemicals and compositions are the advantages of chemical solution deposition (CSD) compared to physical coating methods [12]. According to Nair *et al* [10], the deposition conditions and techniques play a major role in the physical properties of copper oxide thin films. These authors also explained about the annealing effects on copper oxide thin film structural, electrical and optical properties. It was concluded that the annealing of Cu₂O in air at temperature up to 350 °C could cause a conversion of Cu₂O to CuO [13-14]. At higher annealing temperature, total conversion is possible to occur and CuO could revert to Cu₂O. However, this possibility was not further study. Thus, in this paper, Cu₂O thin films were deposited by successively dipping the substrate in a solution of NaOH and in copper complex ion, without the rinsing step between the dipping. The films were annealed in air at temperature ranging from 200 to 400 °C in order to study annealing effects on the growth characteristics of Cu₂O thin film as well as its structural, morphological and optical properties.

2. EXPERIMENTAL

2.1 Film deposition

The chemicals used for the preparation were copper sulfate pentahydrate (Cu₅O₄·5H₂O) of Baker Analyzed Reagent Grade, sodium thiosulfate (Na₂S₂O₃) and sodium hydroxide of analytical grade from Productus Quimicos Monterrey. Microscope slides of 76 × 26 × 1 mm³ were used as substrates for copper oxide film deposition. The copper thiosulfate complex solution was prepared by adding approximately 125 ml of 1 M sodium thiosulfate to 25 ml of 1 M copper sulfate pentahydrate solution until a colorless solution results. Formation of colorless solution could be represented by Eq. (1):



Distilled water was added to the solution to form 250 ml stock solution of the metal ion complex in standard volumetric flask. For deposition purpose, about 80 ml of this solution was transferred to 100 ml beaker and maintained at room temperature. A glass slide used as substrate was first cleaned in acetone and ethanol. The slide was then immersed in 70 °C of NaOH solution by

holding the slide vertically using sample holder. In order to obtain uniform thin films, 20 s of immersion duration was chosen. As a result, OH⁻ ions from NaOH solution adhered to the surface of substrate. Second immersion of the substrate was performed in the copper ion complex solution (prepared in 100 ml beaker). Here again, the immersion period was 20 s. In the solution of thiosulfatocuprate (I), the Cu (I) ions formed by the dissociation equilibrium, $[\text{Cu}(\text{S}_2\text{O}_3)]^- \leftrightarrow \text{Cu}^+ + \text{S}_2\text{O}_3^{2-}$, adhere to the substrate and react with (OH)⁻ ions present on the surface to form Cu₂O by the reaction: $2\text{Cu}^+ + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}$. This completes one cycle of the ion layer adsorption and reaction process. Successive cycles led to thin film deposition. At the end of three immersion cycles, the thin film appeared silvery in reflection. Increasing the number of immersions will increase the thickness of the films. Repeated immersions up to 30 cycles resulted in a film with thickness of ≈ 0.45 μm . The films were washed well with distilled water and dried. For annealing effects investigation, four films were prepared. The films were annealed in air for different temperatures ranging from 200 to 400 °C. Annealing process was done in a furnace with temperature control.

2.2 Characterization

X-ray Diffraction analysis was used as the major tool for identification of phases of the as-prepared copper oxide films. This analysis was done with a Philips X'pert MRD diffractometer with Cu K α radiation ($\lambda = 1.5056$ Å) and a Ni filter. The morphology of the films was observed with scanning electron microscope JEOL F-6400. The absorption spectra of copper oxide thin films were measured by using a UVIKON 923 Double Beam UV-vis spectrophotometer with air as reference. The photoluminescence spectra were measured by using a Perkin Elmer LS55 fluorescence spectrophotometer with an excitation source from Xe lamp in the wavelength range of 450 – 750 nm. The FTIR transmission spectra were recorded using a Nicolet IS 10 spectrophotometer in the spectral range 400 - 2000 cm⁻¹. In order to record infrared patterns, the first copper oxide films on the glass substrates were scratched and copper oxide powder was mixed into KBr powder then a pellet was prepared for each annealed film.

3. RESULTS AND DISCUSSIONS

3.1 Structural properties

XRD patterns of the copper oxide films air-annealed at different temperatures along with that of an as-prepared sample were shown in Fig.1. Well defined peaks at 36.4, 42.3 and 61.3° corresponding to reflections from (111), (200), and (220) planes are observed in Fig.1. This indicates that all samples are polycrystalline and matched the characteristic peaks due to the mineral cuprite, Cu₂O (JCPDS 5-667). Annealing the samples in air at temperature up to 200 °C does not affect the composition of the film. For the sample annealed at 300 °C, Cu₂O (cuprite) become unstable and partially converted to CuO (tenorite). XRD pattern shows an extra peak near $2\theta = 38.7^\circ$ which match reflection from (200) plane of CuO. This pattern shows that in the copper oxide thin films annealed at

300 °C coexist two phases: CuO and Cu₂O. At this temperature, the copper oxide film may not fully oxidize. For the sample annealed at 400 °C, the XRD pattern shows two broad peaks near $2\theta = 35.5$ and 38.7° which match reflections from the (-111) plane and (200) plane respectively attributed to tenorite structure for CuO. The films are converted completely to CuO. In the bulk form, the conversion is reported to take place at temperatures above 400 °C [10]. The conversion of Cu₂O into CuO results from the diffusion of oxygen into the films. Cu₂O starts reacting with O and forms the CuO phase by the following reaction: $2\text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4\text{CuO}$. From thermodynamic considerations, Gibbs free energy of the reaction is around $-3.73 \text{ kcal mol}^{-1}$ for the sample annealed at about 200 °C [10]. Therefore, the formation of the CuO phase at temperature 400 °C can easily be explained by this reaction. The composition CuO is maintained even upon annealing at 400 °C. The sample annealing at 400 °C causes an increase in average crystallite size from 14 to 26 nm. The increase in crystallite size can be attributed to the change in crystallographic phase from Cu₂O to CuO. This relatively small crystallite size in nanometer was due to the low growth rate of copper oxide film.

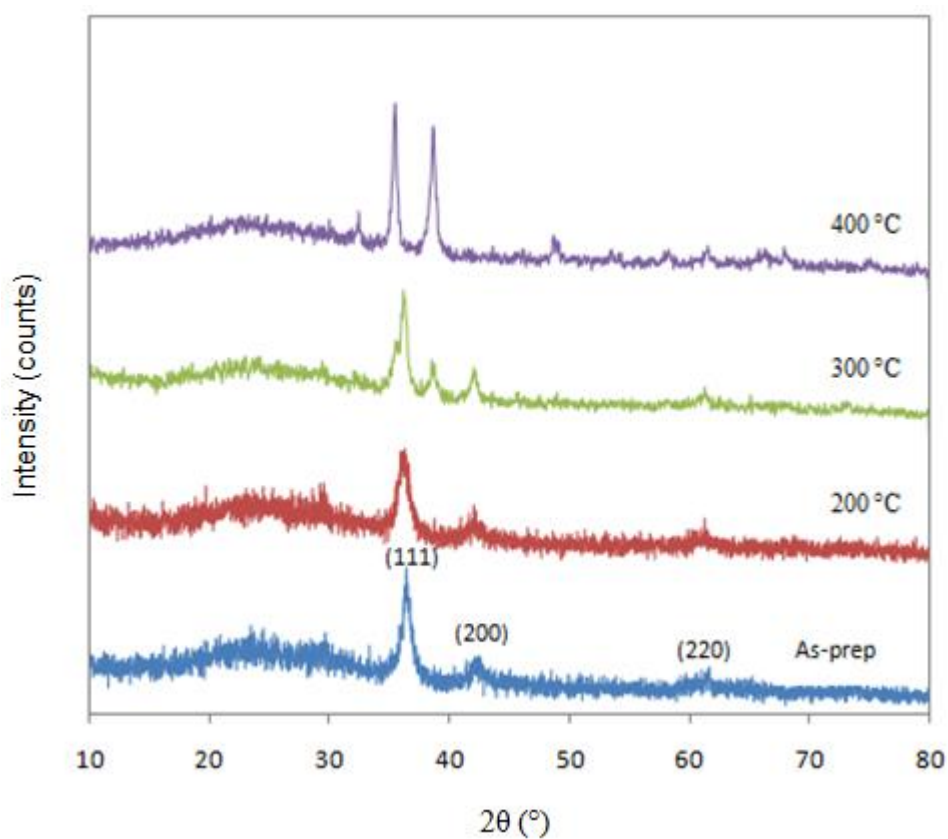


Figure 1. XRD patterns of annealed and reference samples of Cu₂O thin films.

3.2 Morphology and grain size

The microstructure of the films was substantially affected by the annealing temperature. The as-prepared film without annealing has a rough surface and irregular grain size as observed in Fig.2

(a). When the film were annealed at 200 °C, the morphology does not changed much but showed better uniformity in grain size (Fig.2 (b)).

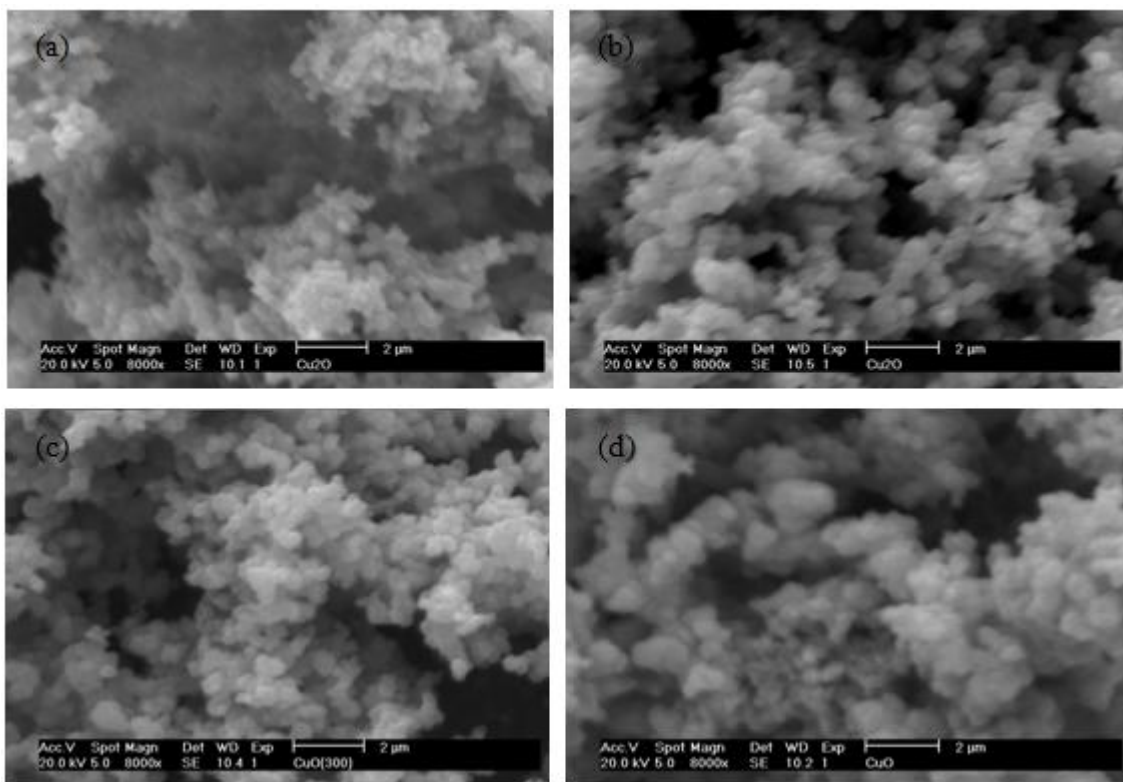


Figure 2. Scanning electron micrograph of Copper oxide thin film (a) as-prepared; (b) annealed at 200 °C; (c) annealed at 300 °C; (d) annealed at 400 °C

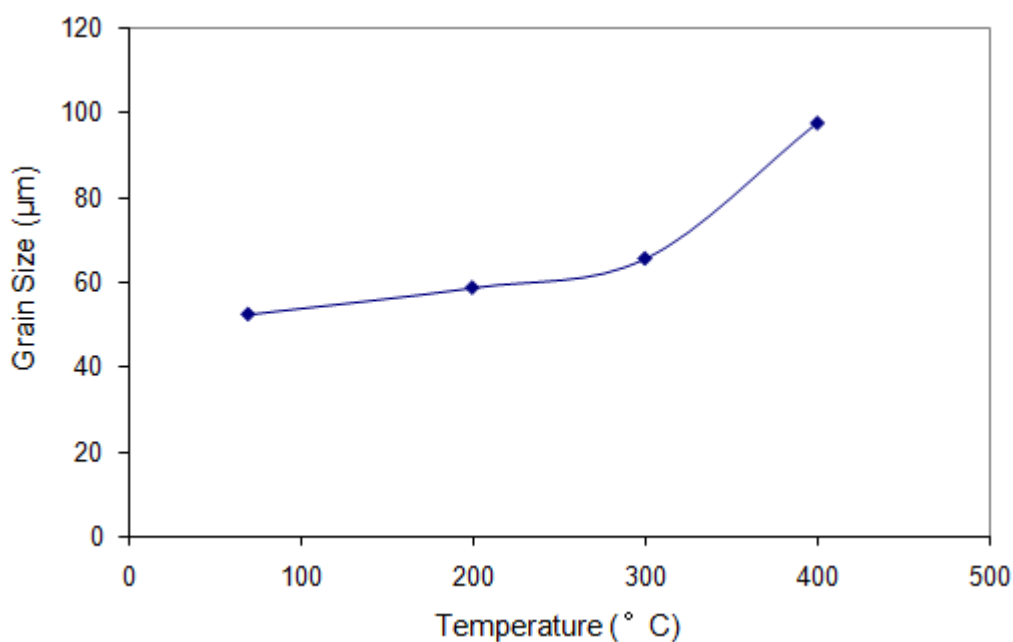


Figure 3. Grain size-temperature curve for copper oxide thin films.

The annealed film at 300 °C shows a continuous and homogeneous granular surface as observed in Fig.2 (c). The SEM for copper oxide annealed at 400 °C showed dense spherical structures and no visible defects indicate that the films are completely converted to CuO. The grain size of annealed film at 400 °C was around 0.9 μm and this is shown in Fig.2 (d). The random distribution of grains, in projection and size, only suggests a random nucleation mechanism and random orientation of grains show that the grain growth is isotropic [13].

The dependence of grain size on temperature is demonstrated in Fig.3, a plot of grain size as a function of temperature for copper oxide thin films. The grain size increased slowly at first (from 52.3 μm to 65.5 μm) whilst the grain size increased more rapidly after that (from 65.5 μm to 97.6 μm). Grain growth rate increases more rapidly at higher annealing temperature. This kinetics of grain growth trend was influenced by the grain size which is in agreement with Huda and Ralph [14].

3.3 Optical properties

3.3.1 UV-VIS

Fig. 4 shows the combination of optical transmittance spectra for all the four samples of copper oxide thin films with 0.45 μm thickness deposited using NaOH solution at temperature of 70 °C. The curves testify that that the film surface is smooth with wavelength longer than 500 nm. As seen from the figure, the curves for oxide film as-deposited and film annealed at 200 °C are distinctly similar. This is due to they have the same composition of Cu₂O (cuprite) structure. The presence of powdery deposit would cause scattering losses from the film surface, which would continuously reduce the transmittance with decrease in wavelength (λ) following an inverse power law, λ⁻ⁿ. However, at the wavelength of about 900nm the transmittance is reduced for oxide films annealed at 300 and 400 °C.

Because of the crystallinity and higher transparency, the copper oxide films are suitable for optical analysis from which the absorption coefficient and energy band gap may be determined. The conversion of Cu₂O into CuO can also be shown by the determination of the optical band gap. For this, in the fundamental absorption region the optical absorption coefficient (α) was evaluated using α = (lnT⁻¹)/t where t is the film thickness and T is the transmittance [4]. The best linear relationship is obtained by plotting α² against hv, based on Eq. (2) below.

$$\alpha hv = A(hv - E_g)^{n/2} \quad (2)$$

where α is absorption coefficient, A a constant (independent from ν) and n the exponent that depends upon the quantum selection rules for the particular material. The photon energy (hv) for y-axis can be calculated using Eq. (3).

$$E = hv = hc/\lambda \quad (3)$$

where h is Plank's constant (6.626x10⁻³⁴), c is speed of light (3x10⁸) and λ is the wavelength.

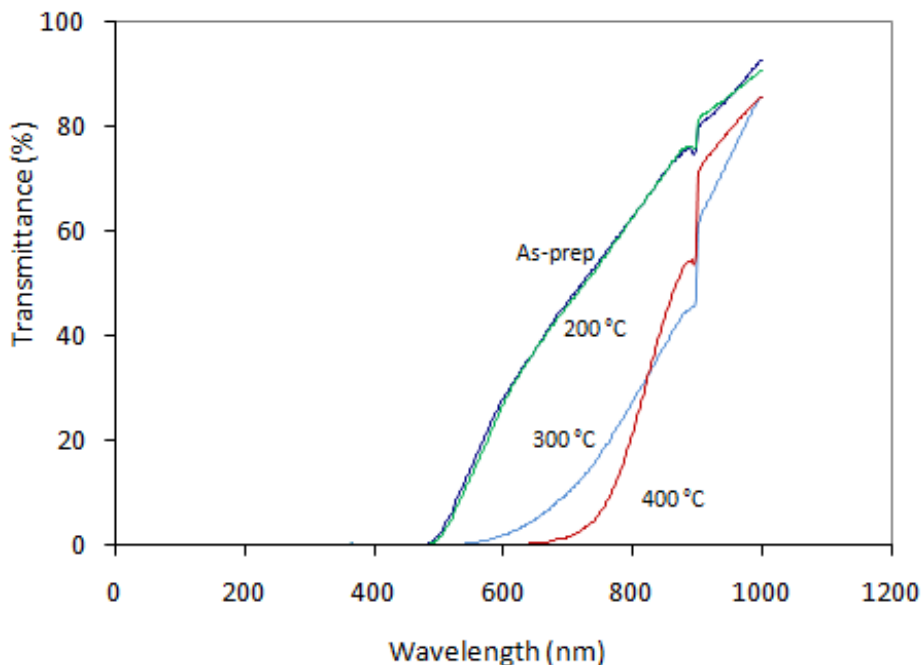


Figure 4. Optical transmittance (T) spectra of annealed and as-prepared thin copper oxide.

A straight line shown in Fig.5 is obtained when α^2 is plotted against photon energy ($h\nu$), which indicates that the absorption edge is due to a direct allowed transition ($n = 1$ for direct allowed transition). The intercept of the straight line on $h\nu$ axis corresponds to the optical band gap (E_g).

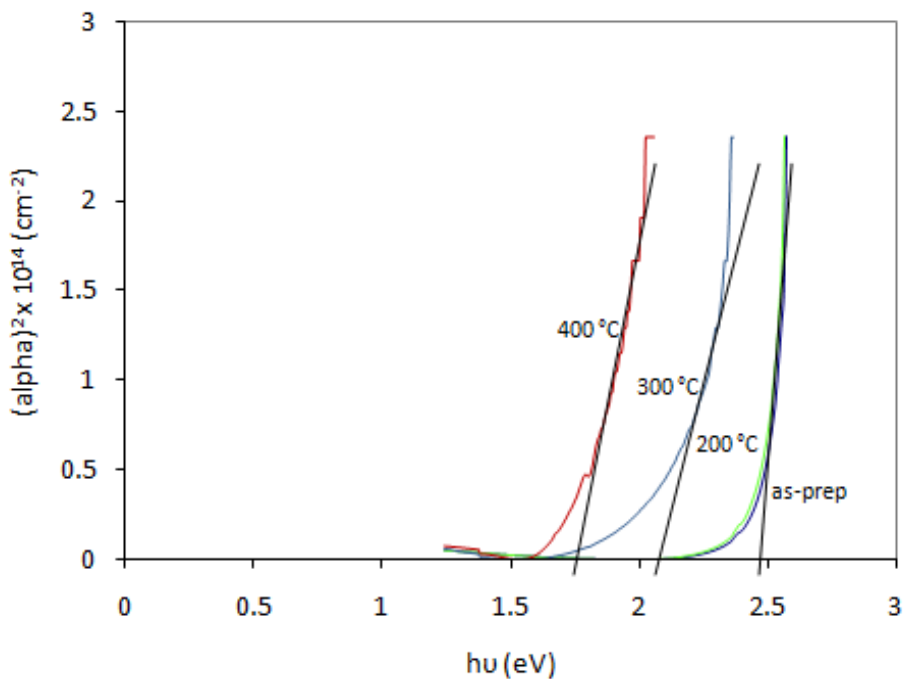


Figure 5. Plot of α^2 versus $h\nu$ curve of annealed and as-prepared thin copper oxide.

The determined optical band gap values for copper oxides are shown in Table 1. The band gaps of films that were obtained after annealing at different temperatures and thus, had different microstructures do not differ significantly. However, the band gap values are in the expected range for copper oxide thin films [5]. In the case of the films annealed in air, the band gap is shifted to lower energies due to change in the composition from Cu_2O to CuO , as shown in Table 1. Both of deposited and annealed films at 200 °C have the same optical band gap at 2.40 eV due to they possess similar cuprite structure with Cu_2O phase. The films annealed at 400 °C and possessing CuO composition show a band gap of 1.73 eV, corresponding to an optical absorption threshold of ~ 900 nm. CuO is the predominant phase after annealing in atmosphere at 400°C. This is in agreement with the XRD results given in Fig. 1. In the film annealed at 300 °C, optical absorption due to the Cu_2O and CuO components are observed, indicated by their respective band gaps (nearly 2.40 and 1.73 eV).

Table 1. Optical band gap (E_g) values for copper oxide thin films

Copper Oxide Thin Films	Energy Band Gap (E_g)
As-deposited	2.40
Annealed at 200°C	2.40
Annealed at 300°C	2.06
Annealed at 400°C	1.73

The lower band gap of the oxide films annealed at 400 °C may indicate better oxidation since the band gap of bulk CuO was reported to be 1.2 – 1.3 eV. Moreover, the CuO films showed another lower energy gap of 1.08 eV. This lower energy gap may be due to absorption involving defect states. The reported values for the band gap of CuO films were 1.73 eV. This scatter in the reported values may be attributed to two factors. First, the optical properties depend critically on the physical properties of the films, which are subsequently affected by the deposition and post-deposition conditions. Second, different models have been used to extract the optical properties from measured quantities. For example, α , α^2 , $(\alpha E)^2$, $(\alpha E)^{2/3}$, and $(\alpha E)^{1/2}$ were all plotted against the photon energy to determine the band gap. This not only affects the value of the band gap but also affects the interpretation of the nature of the gap (i.e. direct or indirect) [15].

3.3.2 Photoluminescence analysis

Photoluminescence analysis in Fig.6 showed a main peak in the visible light band at 360 nm and the band gap energy was estimated to be 3.45 eV. Copper oxide film annealed at 200 °C show intensity at 87. PL intensity is then increased to 137 for oxide film annealed at 300 °C and the intensity is further increased to 177 for film annealed at 400 °C. PL intensity is greatly improved with the increase in annealing temperature and the photoluminescence stability is also improved after annealing.

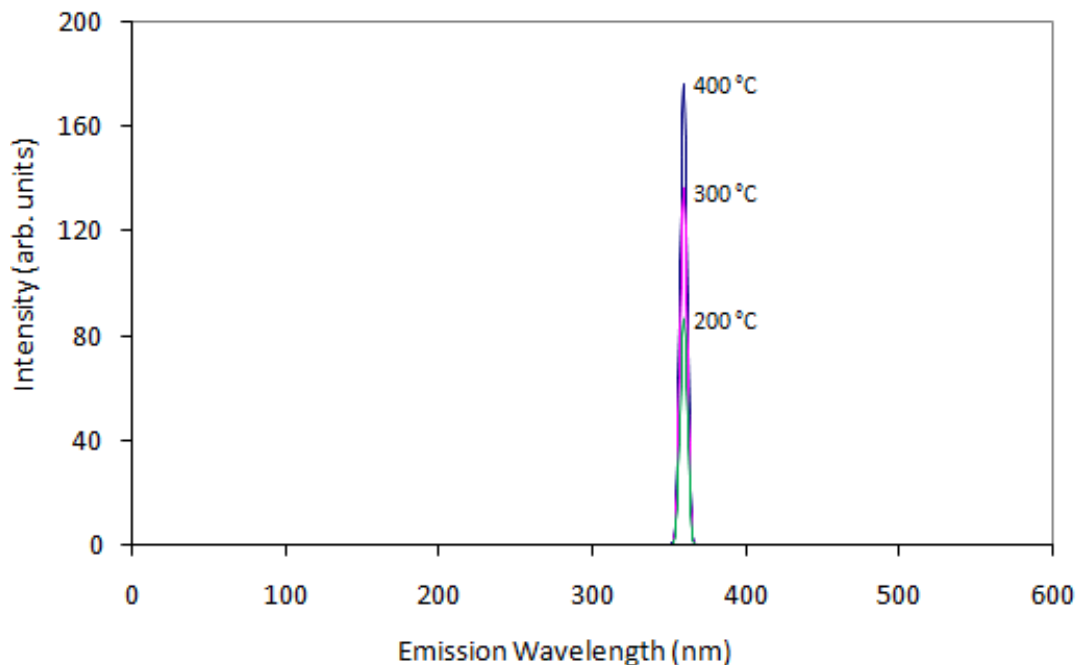


Figure 6. Photoluminescence spectrum of copper oxide thin films annealed at 200 , 300 and 400 °C.

3.3.3 FTIR analysis

The spectra of deposited films shown in Fig.7 (a) and annealed at 200 °C (b) are characterized by a strong band with one transmittance minimum of about 627 and 619 cm^{-1} respectively.

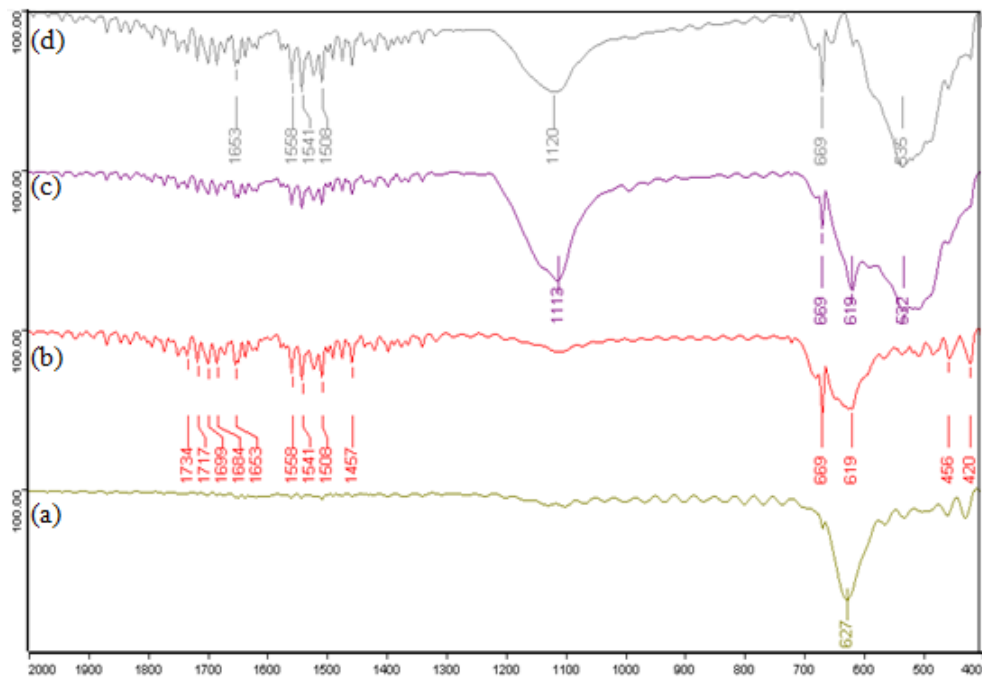


Figure 7. FTIR spectra of copper oxide thin film (a) as-prepared and annealed at various temperatures (°C), (b) 200; (c) 300 and (d) 400.

Balamurugan *et al* [16], and Draou *et al* [17] observed the same band attributed to the stretching of Cu₂O and the spectrum also confirms the absence of CuO where band is around 532 cm⁻¹. For the films annealed at 300 °C (Fig.7 (c)) there are two peaks at wavenumber of about 619 cm⁻¹ (the phonon spectrum of Cu₂O) and 532 cm⁻¹ (the phonon spectrum of CuO). For the films annealed at 400 °C (Fig.7 (d)), broader peaks at about 535 cm⁻¹ are also attributed to the CuO stretching. It is also observed that an obvious peak at about 1120 cm⁻¹ for annealing temperatures after 300 °C. The results of FTIR spectroscopic measurements confirmed the conversion of Cu₂O in to CuO after annealing at 300 °C as peaks associated to Cu₂O was disappeared as shown in Fig.7 (d). There are many non-obvious peaks in the transmittance range from 1300 to 1900 cm⁻¹ which are generated by the noise of the instrument. However their magnitude does not affect in the extraction of safe conclusions.

4. CONCLUSION

Deposition and properties of copper oxide thin films prepared by the successive immersion of glass substrates in solutions of NaOH at 70 °C and of a copper complex (25 °C) have been studied. Single phase Cu₂O thin films with cuprite structure can be easily obtained by using chemical deposition method. The Cu₂O film has mainly (111) and (200) crystalline orientations. Annealing the sample at 200 °C does not affect the composition. At temperature of 300 °C, two phases coexist: CuO and Cu₂O while above 400 °C, CuO prevails.

Microstructure of the films changes on varying film preparation conditions, particularly the annealing temperature. The surface morphology of deposited copper oxide films on glass substrate show grains of micrometric sizes. Each of these grains might correspond to an aggregate of copper oxide crystallites. Kinetic grain growth has been evaluated in copper oxide thin films by the calculation of its grain size at different temperatures. Optical band gap of the films, measured by employing a UV-VIS spectrophotometer, lies at 1.73 - 2.40 eV. Hence, the films of copper oxide obtained by this method may be exploited as cheap and efficient solar light absorber. Furthermore, annealing of copper oxide thin film at appropriate temperature can enhance the photoluminescence behaviors. FTIR spectroscopic measurements further proved that the conversion from Copper (II) oxide into Copper (I) oxide after annealing the films at 300 °C.

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