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Effect of oxidation temperature on the properties of copper oxide thin films prepared from thermally oxidised evaporated copper thin films

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Abstract**:** *Copper thin films were deposited on glass substrates using thermal vacuum evaporation at 100 ^oC substrate temperature and then thermally oxidized in air at varying temperatures of 150 ^oC, 250 ^oC, 35 0 ^oC and 450 ^oC for 2h each. The structural, electrical, and optical properties of the film are determined using X-ray diffraction (XRD), scanning electron microscopy (SEM), four point probe and UV-visible spectroscopy. The XRD pattern show the formation of fine grain Cuprous Oxide (Cu_2O) at 250 ^oC and Cupric Oxide CuO at 350 and 450 ^oC. Resistivities were calculated to be 4.1x10^{-6} Ω-cm, 1.92x10^{-6} Ω-cm, 1076.76 Ω-cm, 127.51 Ω-cm and 205.16 Ω-cm for the as-deposited and Cu Films oxidised at 150, 250, 350 and 450 ^oC respectively. The Optical band gap value varied between 1.78 eV and 2.2 eV.*

Keywords- *Cupric oxide, Cuprous oxide, Optical band gap, Thermal oxidation, X-ray diffraction,*

I. Introduction

Copper oxides are semiconductors that have a natural abundance of starting material (Cu). They are non-toxic and are easily obtained by oxidation of Cu. Copper oxide thin films have potential applications in areas such as photovoltaics and electronic device fabrication [1, 2, 3]. Copper oxide has two major types, cuprous oxide (Cu_2O) and cupric oxide (CuO). Cuprous oxide (Cu_2O) belongs to the space group Pn3m, and its unit cell has two copper and four oxygen ions. These are arranged with oxygen atoms in a cubic lattice structure surrounded tetrahedrally by copper ions [4]. Cupric oxide (CuO) has a monoclinic crystal structure in which each Cu has four oxygen neighbours [5]. These two close copper oxides show distinct XRD spectra. They have good electrical and optical properties. The band gap energy for the semiconductors is typically in the range 1.21-2.1eV for CuO [6, 7] and 2.1-2.6eV in Cu_2O [6].

Different physical and chemical techniques have been utilized to grow copper oxide thin film on glass including sputtering [6], electrodeposition [8], SILAR [9], chemical deposition [10] and spray pyrolysis [7]. In this work, we investigated the effect of temperature of oxidation on the properties of copper oxide thin film prepared by oxidation of thermal vacuum evaporated Cu thin films. The films were characterized using scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), UV-Vis spectrophotometer and four point probes for electrical characterization.

II. Experiment Details

Copper thin films were deposited by thermal vacuum evaporation on a glass substrate at a vacuum pressure of 1.6x10^{-5} torr and 100 ^oC substrate temperature. The thermal evaporator used was an EDWARD FL 400 AUTO 306 evaporator equipped with SQC-310C deposition controller. Copper pellets of 4N grade was used and evaporated from a molybdenum boat. Thermal oxidation of the Copper thin films was achieved using a horizontal Carbolite 201 tubular furnace in open air at temperatures of 150 ^oC, 250 ^oC, 350 ^oC and 450 ^oC for two hours each.

The as-deposited and thermally oxidized films were characterized with a PANalytical XPERT-PRO MPD X-ray diffractometer operated with a Cu Kα radiation source at a voltage 40kV and a wavelength of 1.54060Å. The films morphology and composition was analyzed with a CARL ZEISS MA 10 scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) system ISIS 300 oxford coupled to the SEM. Optical transmittance was measured with a UV-visible spectrophotometer (AVASPEC 2048) in the wavelength range 190 - 900 nm. The thickness of the thin film was determined by VEECO DEKTAK 150 profilometer and they were electrically characterized using four point probe. The samples were labeled Cu_as-deposited for as deposited Cu film and Cu_150, Cu_250, Cu_350 and Cu_450 for Cu films oxidised at 150, 250, 350 and 450 ^oC.

III. Results And Discussion

3.1 Structural properties

The X-ray diffraction pattern of the as-deposited copper and thermally oxidised copper at varying temperatures of 150 ^{o}C, 250 ^{o}C, 350 ^{o}C and 450 ^{o}C films are shown in Fig. 1. The as-deposited copper sample revealed diffraction peaks at 2θ equal to 43.20^{o} and 50.50^{o}, these correspond to the crystallographic reflection of (111) and (200) planes of metallic Cu, with lattice constant a_o of 3.61306Å which matched with powered diffraction reference code 03-065-9026 of standard Cubic Cu phase. Oxidation of Cu thin film at 150 ^{o}C still shows purely metallic Cu phase similar to as–deposited copper. For sample copper film oxidised at 250 ^{o}C, there is a diffraction peaks at 36.46^{o} and correspond to the (111) reflection plane of Cu_2O (ICSD reference code 01-071-4310) in agreement with [14, 15]. XRD pattern for copper sample oxidised at 350 ^{o}C shows strong peaks at 2θ of 35.47^{o} and 38.65^{o}, these peaks correspond to reflection planes ($\bar{1}$11) and (111) of monoclinic CuO phase identified from the standard data ICSD reference code 01-089-2530. The sample also exhibits very weak reflection planes at 32.23^{o} and 48.71^{o} belonging to (110) and ($\bar{2}$02) planes of CuO. No other reflection peaks were observed, showing the transformation of Cu_2O to CuO at 350 ^{o}C and it agrees well with similar pattern reported [16]. The formation of CuO at 350 ^{o}C is reasonable since the phase diagram of Cu-O system show stable CuO phase at 300 ^{o}C even at low oxygen partial pressure [17].

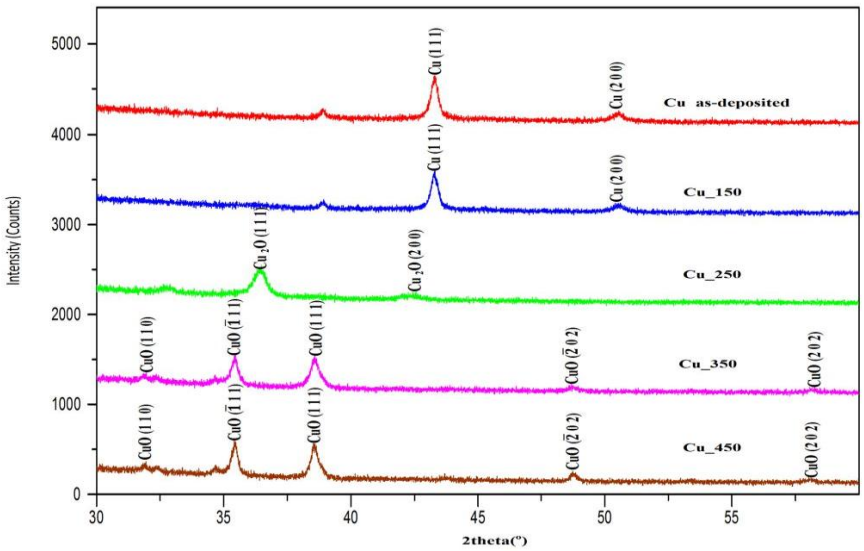


Figure 1. XRD pattern of Copper oxide films as a function of oxidation temperature

The XRD spectra of sample copper oxidised at 450 ^{o}C shows strong diffraction peaks at 35.44^{o} and 38.53^{o}, these are attributed to the reflection of ($\bar{1}$11) and (111) crystallographic planes of CuO and the weak peaks at 32.54^{o}, 48.74^{o} and 58.36^{o} are due to (110), ($\bar{2}$02) and (202) planes of CuO phase which marches the ICSD reference code 01-073-6023 and it tallies with the work reported [12]. The low crystallinity of the particles of the films is reflected in substantial broadening of peaks for all the samples.

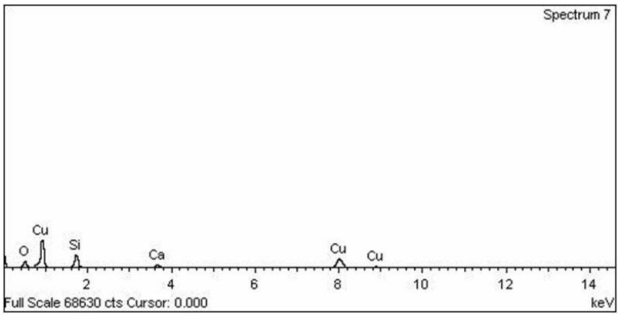
The grain sizes were estimated for all the samples using Debye-Scherrer`s formula [2, 8],

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

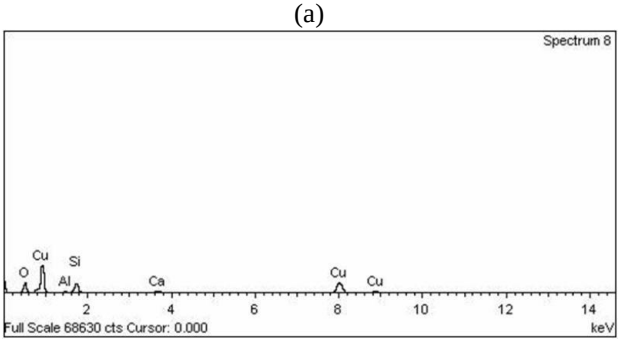
where λ is the wavelength of the X-ray, β full width at half maximum (FWHM) and θ is the diffraction/Bragg`s angle. The grain size calculation from the XRD analysis are 6.7nm, 18.95nm, 4.6nm, 4.6nm and 11.5nm, for as deposited films and Cu_150, Cu_250, Cu_350 and Cu_450 films respectively.

3.2 Composition

Chemical characterisation was conducted on the films using the EDX and is shown in Fig. 2. The EDX spectrum of the obtained Cu_2O films in Fig. 2(a) and CuO films in Fig. 2(b) reveals the presence of copper and oxygen and other elements from the glass substrate.



(a)



(b)

Figure 2. EDX spectrum of (a) Cu_2O film and glass substrate (b) CuO and glass substrte

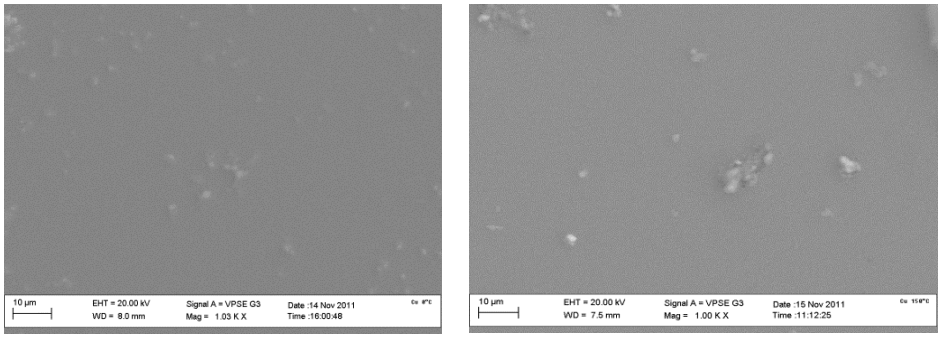
The EDX analysis in Table 1 show elemental composition of 84.6 % of Cu and 15.5 % of O for Cu_250 film. This is close to the stoichiometric composition for Cu_2O (88.91 % Cu and 11.18% O). The elemental composition of Cu_350 and Cu_450 are 71.5 % and 71.3 % for Cu respectively and 28.5 % and 28.7 % for O respectively. These are also close to the stoichiometric composition of CuO (79.88 % Cu and 20.12 % O).

Table 1. EDX elemental analysis of samples oxidised at 250, 350 and 450 ^oC

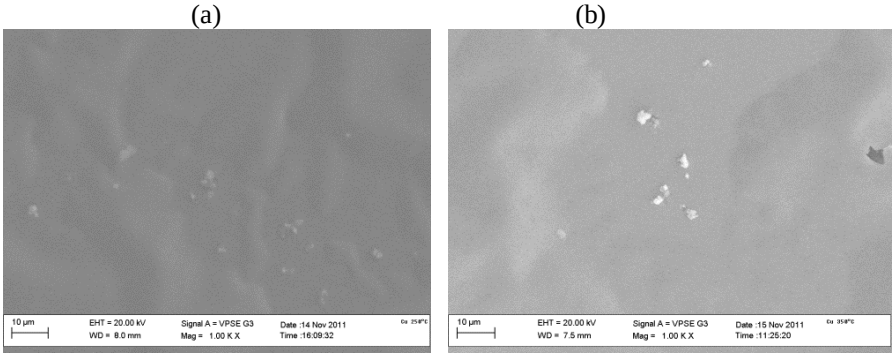
Sample	Cu %	O %
Cu_250	84.6	15.5
Cu_350	71.5	28.5
Cu_450	71.3	28.7

3.3 Surface Morphology

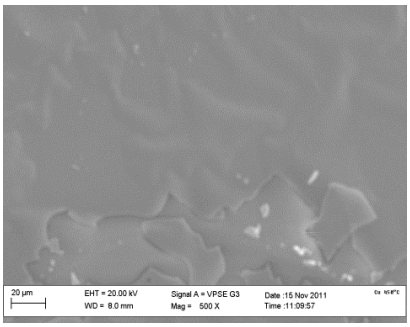
The surface morphology of the sample Copper thin film as-deposited and Cu_150, Cu_250, Cu_350 and Cu_450 films examined by SEM are shown in Fig.3. In Figure 3a, the as-deposited sample show smooth coating of copper on the substrate with dense uniform tiny grains. The film had a metallic-brown color of Cu. The copper thin film oxidised at 150 ^oC for 2h also show a smooth surface with well packed tiny grains and a few irregular shaped protrusions. The surface of the sample turned black but with a hue of reddish brown underneath, denoting partial oxidation of the film. At 250 ^oC and 350 ^oC the sample surface is swollen showing a detachment of the film from the substrate. The sample oxidised at 450 ^oC, have swollen part breaking off. This is as a result of high stresses in the film that can lead to peeling off from the substrate.



. (a) (b)



(c) (d)



(e)

Figure 3. SEM image copper (a) as-deposited, (b) Cu film oxidized at 150 ^{o}C, (c) Cu film oxidized at 250 ^{o}C, (d) Cu film oxidized at 350 ^{o}C and (e) Cu film oxidized at 450 ^{o}C

3.4 Optical properties

Fig. 4 Show the reflectance spectra of films oxidized at 250, 350 and 450 ^{o}C. The the films had reflectance lower than 40% in the UV and visible region with Cu_250 having the highest reflectance, while the film deposited at 350 ^{o}C had the lowest. The surface roughness of the films influences the reflectance spectra, and higher surface roughness gives rise to lower reflectance [12]. In the near IR region the reflectance is higher and approaches 80% for Cu_250 and Cu_450. The optical reflectance spectra of CuO and Cu_2O films can be considered as a key parameter in feasibility investigation of CuO and Cu_2O films for solar cell applications and plays a key role on energy conversion efficiency of solar cells.

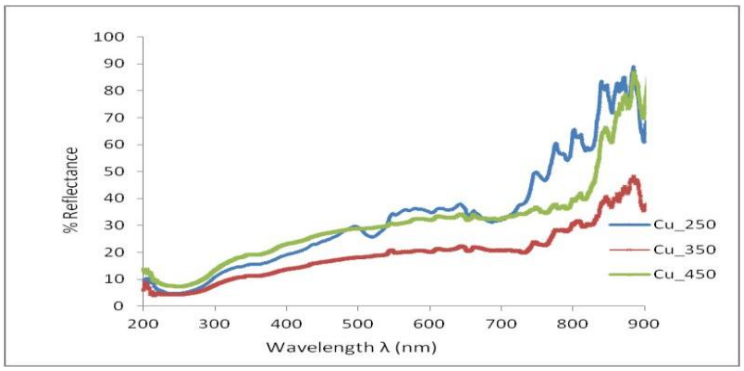


Figure 4. Reflectance spectra of Copper oxide films oxidised at 250, 350 and 450 ^{o}C

The optical band gap values was computed using result from the optical transmittance measurements, the band gap values were obtain by linear extrapolation of the graph of $(\alpha h\nu)^2$ versus hγ curves based on the Tauc`s relation [4,11] below.

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

As shown in Fig. 5 the band gap value for film prepared at 250 ^{o}C oxidising temperature are obtained as 2.2 eV, 1.78 eV for film oxidised at 350 ^{o}C and 1.80 eV for film oxidised at 450 ^{o}C. Cu_350 and Cu_450 exhibit sharper optical band gap edge than the Cu_250 film. The high band gap Cu_2O layers are employed in the top layers of solar cells while low gap CuO layers can be used as the absorption layers of solar cells. The metallic Cu as-deposited and Cu_150 had poor transmittance and quite undistinguishable absorption edge; as such their band gap could not be estimated.

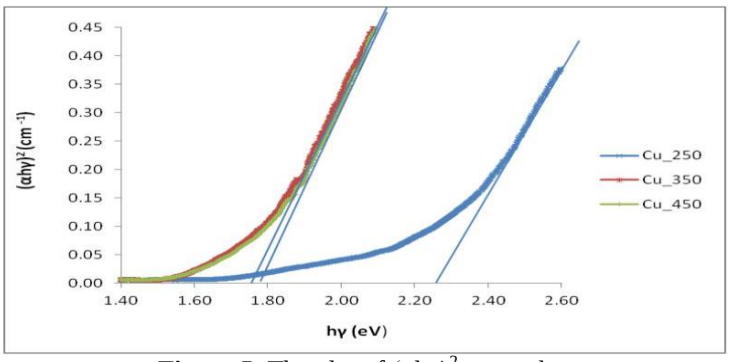


Figure 5. The plot of $(\alpha h\gamma)^2$ versus hγ

3.5 Electrical Characteristics

The electrical resistivity and sheet resistance of the samples are shown in the Table 2. The as-deposited sample and sample copper oxidized at 150^{o}C shows very low resistance and resistivity values which confirm copper in its metallic form. At the end of the oxidation treatment, the resistivities changes to higher value.

TABLE 2. Grain size, resistivity and optical band gap of samples

sample	Grain size (nm)	Resistivity(Ω-cm)	Band gap (eV)
Cu_as-deposited	6.70	4.10×10^{-6}	-
Cu_150^{o}C	18.95	1.92×10^{-6}	-
Cu_250^{o}C	4.60	1076.76	2.20
Cu_350^{o}C	4.60	127.51	1.78
Cu_450^{o}C	11.50	205.16	1.80

IV. Conclusion.

Copper Thin films on glass substrates were formed by thermal vacuum evaporation method at 100 ^{o}C substrate temperature. Copper oxide were prepared by annealing the copper thin film in a furnace in open air at varying temperatures of 150 ^{o}C, 250 ^{o}C, 350 ^{o}C and 450 ^{o}C. XRD, SEM and EDX confirms the crystal structure of copper oxide, its surface morphology shows colour changes that match reported literatures and the elemental compositions which indicated presence of copper and oxygen. The low values of electrical resistivities of the as-deposited copper film and copper film oxidised at 150^{o}C were 4.1 x 10^{-6} Ω-cm and 1.92 x 10^{-6} Ω-cm respectively. For higher temperature oxidations at 250^{o}, 350^{o} and 450^{o}, the resistivity values were 1076.76 Ω-cm, 127.51 Ω-cm and 205.16 Ω-cm respectively, which is well within the semiconductor values. Optical band gap values of the films, measured by employing a UV-vis spectrophotometer, were 2.2 eV for cuprous oxide, and for cupric oxide 1.78 and 1.80 eV.

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