

**COMPARATIVE STUDY OF  $Cu_xS$  and  $Cu_ySe$  THIN FILMS GROWN BY CBD**

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Chalcogenide thin films of  $Cu_xS$  and  $Cu_ySe$  were grown on glass substrates using the chemical bath growth technique. The bath precursors for the synthesis of the  $Cu_xS$  include thiourea ( $(NH_2)_2SC$ ), ammonium hydroxide ( $NH_4OH$ ) solution and triethanolamine, TEA ( $N(CH_2CH_2OH)_3$ ) while those for the preparation of the  $Cu_ySe$  thin are sodium selenosulphate solution ( $Na_2SeSO_3$ ) and ammonium hydroxide ( $NH_4OH$ ) solutions. Copper II dihydrate ( $CuCl_2 \cdot 2H_2O$ ) was used as the starting material in each case. The effects of thermal treatment on the structural and spectral properties of the thin films were studied using X-Ray diffractometer and UV-VIS spectrophotometer respectively. The structural studies show the presence of chalcocite ( $Cu_{1.96}S$ ) and digenite ( $Cu_9S_5$ ) phases with average grain size of 13.39nm for  $Cu_xS$  thin films. Tetragonal  $Cu_3Se_2$  (umangite) and cubic  $Cu_2Se$  with average crystallite size of 35.79nm were observed for the  $Cu_ySe$  thin films. The optical band gap energy for the  $Cu_xS$  thin films is between 2.30eV and 2.45eV while the band gaps of the  $Cu_ySe$  thin films fall between the range 1.80eV and 1.95eV. Unlike the  $Cu_xS$ , the XRD analysis also revealed that thermal treatment significantly improved the crystalline structure of the  $Cu_ySe$ .

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**1. Introduction**

Nanoscience and Nanotechnology involve research to study the behaviours and properties of materials with dimensions at the nanoscale. It is relatively a new field that has generated excitement worldwide. Nanoscience and nanotechnology is aimed at studying, creating or applying materials, devices and systems that could control matter at nanometric or even atomic scale (Vida-Smitit et al, 2004). This field of study promises to improve lives and contribute to economic growth (Michael, 2002; Bürgi and Pradeep, 2006). One of the interesting features of researches in nanotechnology is that at nanoscale, some materials may have unique properties different from those of the bulk crystalline materials. Such properties could make the materials very attractive in so many technological applications such as in optoelectronic devices, optical communications, solar control devices and photovoltaic solar cell fabrication (Garcia, 1999; Pathan and Lokhande, 2004; Adam et al., 2008; Eya, 2006).

Copper selenides and copper sulfides are among the chalcogenide compounds with several applications in Nanosciences. They have been found very useful in coating solar energy conversion systems and solar control devices (Bari *et al.*, 2009; Pathan and Lokhande, 2004). The chalcogenides are also known to be used in the fabrication of microelectronic devices, optical filters as well as in low temperature gas sensor applications (Savadogo, 1998; Teteris, 2003; Ilenikhena, 2008). In addition, ternary copper chalcogenides like copper indium diselenide, and copper indium gallium selenides, in recent times, are now widely used in the fabrication of solar photovoltaic cells (Merrigan, 1982; Markvart Tomas, 1992; Sharin *et al.*, 2007; Al-Mamun *et al.*,

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2005; Mane *et al.*, 2006; Bari *et al.*, 2009; Pathan *et al.*, 2003; Kim *et al.*, 2002; Garcia *et al.*, 1999). The p-type copper selenide thin films can exist in either stoichiometric ( $\alpha$ -Cu<sub>2</sub>Se, CuSe, Cu<sub>3</sub>Se<sub>2</sub> and CuSe<sub>2</sub>) or non stoichiometric (Cu<sub>2-x</sub>Se) forms (Garcia *et al.*, 1999). Special attention is now given to the study of copper sulfide thin films probably due to the discovery of the CdS/Cu<sub>x</sub>S heterojunction solar cell (Pathan and Lokhande, 2004). At least five stable phases of the copper-sulfur system are naturally known to exist. Among these include *covellite* (Cu<sub>1.00</sub>S), *anilite* (Cu<sub>1.75</sub>S), *digenite* (Cu<sub>1.80</sub>S), *djurleite* (Cu<sub>1.97</sub>S), and *chalcocite* (Cu<sub>2.00</sub>S) (Pathan and Lokhande, 2004; Evans, 1981). Other phases that exist include *yarowite* (Cu<sub>1.12</sub>S) and *spionkopite* (Cu<sub>1.14</sub>S) (Goble, 1985). This paper presents the comparative study of copper sulphide and copper selenide thin films grown by chemical bath deposition technique.

## 2. Experimental procedure

### *Synthesis of the copper sulfide and the copper selenide*

The thin films of copper sulfide were obtained by first preparing one molar solution of copper II dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O) solution, thiourea (NH<sub>2</sub>)<sub>2</sub>SC, 25% ammonium solution (NH<sub>4</sub>OH) and triethanolamine TEA (N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub>). 10ml of the TEA, 10ml of the thiourea, 10ml of the ammonium solution and 30ml of distilled water were respectively added to 3ml of the copper chloride solution in a 50ml beaker and then gently stirred at room temperature to obtain a homogenous solution. The complexing agent, TEA was used in order to obtain high quality films (Nair *et al.* 1987; Ortega-Borges *et al.*, 1993; Nascu and Popescu, 2004) by ensuring the slow release of the metallic ions in the solution and slow precipitation of the compound. The CuCl<sub>2</sub>·2H<sub>2</sub>O solution and the (NH<sub>2</sub>)<sub>2</sub>SC were used as the sources of the Cu<sup>2+</sup> and the S<sup>2-</sup> ions respectively.

Similarly, the starting material for the chemical bath solution used in preparing the copper selenide thin films was copper chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O). Other precursors include selenium powder, anhydrous sodium sulphite (Na<sub>2</sub>SO<sub>3</sub>) and ammonium hydroxide (NH<sub>4</sub>OH) solutions which served as the complexing agent. 5g of the selenium powder, which ordinarily is not soluble in water, and 25g of sodium sulphite were added to 250ml of distilled water. The mixture was continuously stirred using a magnetic stirrer at 65°C for three hours, when it became a clear solution and allowed to cool. 5ml of the resulting sodium selenosulphate solution (Na<sub>2</sub>SeSO<sub>3</sub>) was added to 10ml, 1M CuCl<sub>2</sub> solution, 10ml, 25% NH<sub>3</sub> and 30ml of distilled water. The bath was also prepared in a 50ml beaker. The Na<sub>2</sub>SeSO<sub>3</sub> was the source of the selenium ions (Se<sup>2-</sup>) while the copper chloride in the solution provided the copper ions (Cu<sup>2+</sup>).

In a saturated bath solution, the ionic product is equal to the solubility product. But when the ionic product exceeds the solubility product, the solution becomes supersaturated and precipitation occurs with subsequent combinations of ions on the substrate and in the solution to form nuclei. Therefore, for thin film deposition to occur successfully, the ionic product must exceed the solubility product (Pathan and Lokhande, 2004). The state of the substrate's surface greatly affects the growth of the deposited films. Hence it is very important to clean the surface of the substrates (El-Nahass *et al.*, 2001; Thomas and Mark, 2002). The glass substrates, with dimensions 7.5mm X 2.6mm X 1.0mm, were degreased in HCl for two days, washed with detergent solution and rinsed in distilled water. They were subsequently dipped into acetone and ethanol for 30 minutes respectively, rinsed in distilled water and allowed to dry. These substrates were then vertically suspended into the beaker containing the bath solutions. The optimum deposition time for the copper sulfide was 2 hours 20 minutes at 60°C while the copper selenide thin films deposited at room temperature for 15 hours. Both samples adhered strongly to the substrates. In each case, a sample (X1 for copper sulfide and Y1 for copper selenide) was left as-grown while the others (X2, X3 for copper sulfide and Y2, Y3 for copper selenide) were annealed at 100°C and 400°C respectively.

### 3. Characterizations

Information about the optical and structural properties of semiconductor materials may be obtained when they are allowed to interact with electromagnetic radiations and the resulting radiation analyzed and interpreted. The structural studies for the thin film samples were characterized with X-ray diffractometer using Cu  $K_\alpha$  radiation with wavelength,  $\lambda = 1.54056\text{\AA}$ .

The spectral absorbance and transmittance of the chemical bath deposited thin films were measured at room temperature using the Unico–UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1100nm. Based on the optical theoretical relationships, the spectra data was employed to evaluate the reflectance, absorption coefficient, optical band gaps, refractive indices and optical conductivities. The XRD data was used to determine the phases of the deposited thin films and to estimate their crystallite sizes.

### 4. Results and discussion

#### 4.1 Structural Analysis

##### *XRD Spectra*

Figs. 1 and 2 show the respective XRD patterns for the copper sulfide and copper selenide thin films. The observed XRD patterns of the as-grown copper sulfide thin films (X1) shows the presence of mineral structure, *chalcocite* (JCPDS file No. 29-0578),  $\text{Cu}_{1.96}\text{S}$  with corresponding diffraction  $2\theta$  peak angles of  $31.94^\circ$  and  $70.77^\circ$ . The  $(h\ k\ l)$  planes responsible for the diffractions are  $(0\ 0\ 4)$  and  $(1\ 0\ 8)$  with respective full-width-at-half-maximum (FWHM) of 1.9000 and 1.0343. Analysis for the sample annealed at  $400^\circ\text{C}$  (X3) revealed the compound, *digenite*,  $\text{Cu}_9\text{S}_5$  (JCPDS file No. 26-0476) with standard diffraction angles  $26.29^\circ$ ,  $29.31^\circ$ ,  $32.20^\circ$  and  $40.07^\circ$ . The  $(h\ k\ l)$  planes responsible for these diffraction patterns are  $(1\ 0\ 1)$ ,  $(1\ 0\ 7)$ ,  $(1\ 0\ 10)$  and  $(1\ 0\ 16)$  with respective FWHM of 1.0689, 1.0858, 1.0544 and 1.0351. The as-grown and the annealed thin films have average crystallite sizes of 12.55nm and 14.22nm respectively.

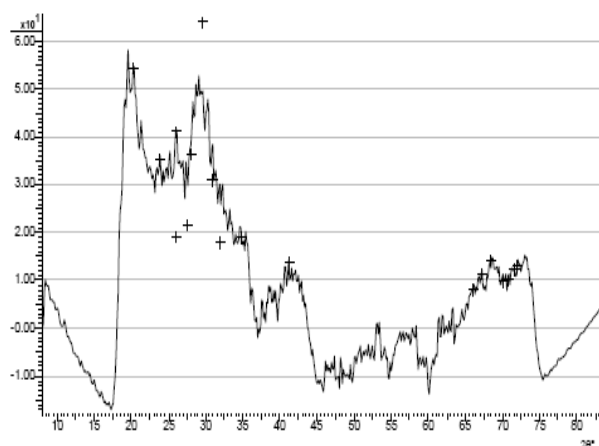


Figure 1a: XRD pattern of the as-deposited copper sulfide thin films(X1).

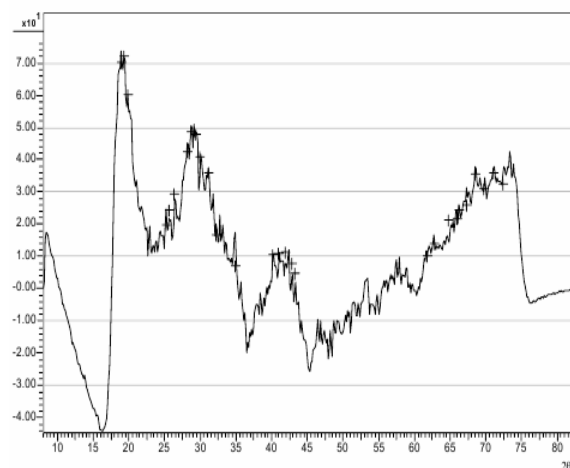


Figure 1b: XRD pattern of the copper sulfide thin films annealed at  $400^\circ\text{C}$  (X3.)

The copper selenide thin films were identified structurally as tetragonal  $\text{Cu}_3\text{Se}_2$  (*umangite*) for the as-grown (Y1) and cubic  $\text{Cu}_2\text{Se}$  for the annealed sample (Y3) with average crystallite sizes of 32.618nm and 38.955nm respectively. The peaks of the as-deposited thin films were not as distinct as that annealed at  $400^\circ\text{C}$ . The most prominent peaks for the annealed copper selenide were observed at standard diffraction angles  $2\theta = 24.82^\circ$  and  $51.94^\circ$  corresponding to full-width-

at-half-maximum (FWHM), 0.40219 and 0.39246 respectively. The preferred orientations of the films correspond to (2 2 1) and (3 1 1) planes respectively.

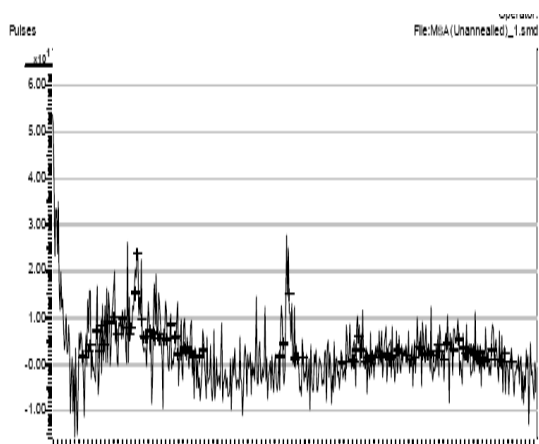


Fig. 2a: XRD pattern of the as-deposited CuSe thin films

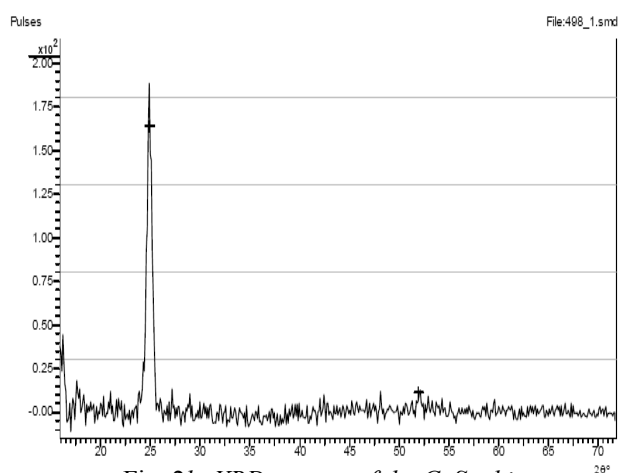


Fig. 2b: XRD pattern of the CuSe thin films annealed at 400°C

In accordance with report (Al-Mamun *et al.*, 2005), the annealed films revealed well defined peaks with high intensities suggesting the formation of crystalline films at higher annealing temperatures. This is unlike the copper sulfide thin films in which the annealing process did not significantly improved the crystalline nature of the films.

## 4.2 Optical properties

### Band gap study

The optical band gaps  $E_g$  for materials are related by the expression (Merrigan, 1982):

$$\alpha = \left( \frac{A}{hv} \right) (hv - E_g)^{n/2}, \quad (1)$$

where  $h$  and  $\nu$  represent the Planck's constant and the frequency of the incident photons respectively. The values of the band gaps are then determined from the variation of  $(\alpha hv)^{2/n}$  with the incident photon energy ( $h\nu$ ). Figure 3 (a, b and c) are the plots of  $(\alpha hv)^2$  against  $h\nu$  for allowed direct transition where  $n = 1$ . The band gaps of the copper sulfide thin films were found to be within the range 2.30eV and 2.45eV. These are comparable to values in earlier reports (Pathan and Lokhande, 2004; Ilenikhena, 2008; Popovici *et al.*, 2009; Uhuegbu, 2010). However, Valentina and Mindaugasand (2009) reported indirect band gaps of 1.25eV and 1.3eV for copper sulfide layers on a polyamide films, whereas, the indirect band gap in this case (data not shown) fall between 1.0 and 1.4eV. Materials with such indirect wide optical band gap energy may possibly be used in the fabrication of light emitting diodes as well as in electroluminescent display (Richard, 1978; Uhuegbu, 2010; Pawan *et al.*, 2006). The copper selenide thin films has lower direct optical band ranging between 1.80eV and 1.95eV which are fairly comparable with reports for thin films deposited using different techniques (Sharin *et al.*, 2007; Al-Mamun *et al.*, 2005; Bari *et al.*, 2009; Pathan *et al.*, 2003). The optical band gap of the copper selenide is sufficiently large and could be employed in the design of the transparent upper layer in hetero-junction solar cell (Neville, 1978).

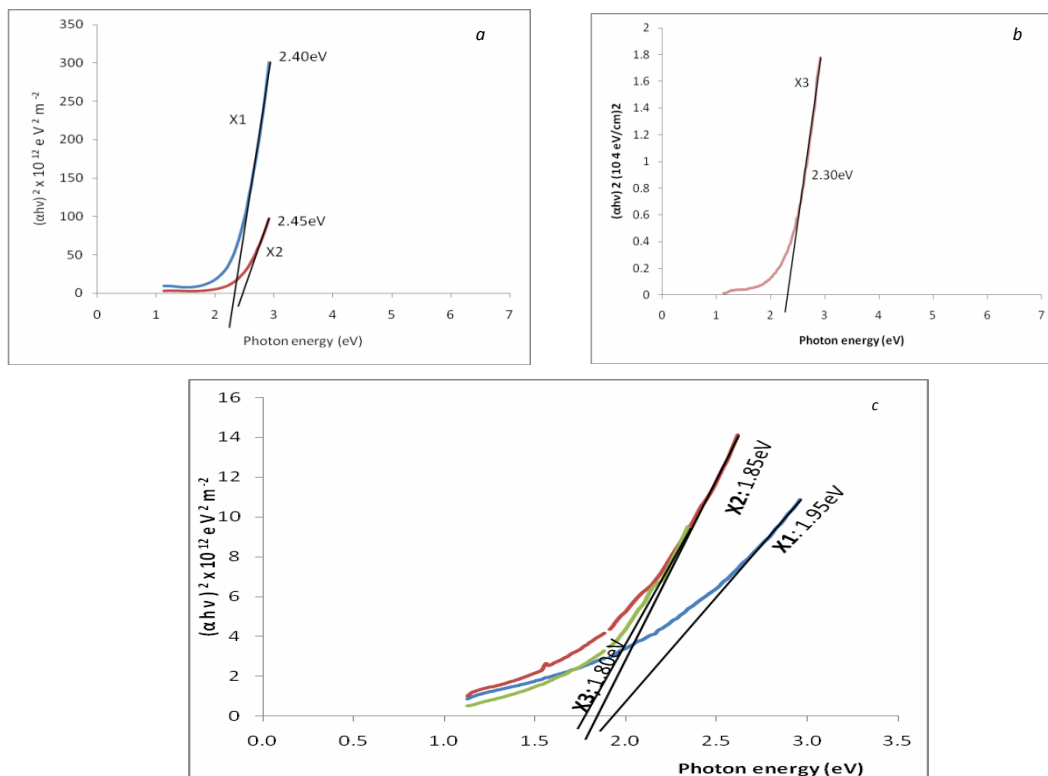


Figure 3 (a,b,c): Plot of  $(\alpha h\nu)^2$  as a function of photon energy ( $h\nu$ ) for the copper sulfide (X) and copper selenide (Y) thin films

#### Absorbance and transmittance

Both the copper sulfide and the copper selenide thin films revealed high absorbance in the UV and the visible regions with gradual decrease towards the NIR region of the electromagnetic spectrum. The plot of absorbance vs photons wavelength (figure 4 a) shows that copper selenide thin films have relatively higher absorbance than the copper sulfides. However the copper sulfide showed more remarkable response to thermal treatment. Sample X3 which was annealed at 400°C displayed the least absorbance. Conversely, all the thin films have very low transmittance near the ultra-violet regions. The values increased towards the longer wavelengths of the spectrum. In addition, the copper sulfide annealed at 400°C here shows the highest value of transmittance (~90%). Both the copper sulfide and copper selenide thin films show relatively low reflectance, below 25% (data not shown). Moreover, reflectance of the copper sulfide, X3 annealed at 400°C is below 10% in all the regions. Consequently, the thermally treated copper sulfide could serve as good material for anti-reflection coating and could also be used in solar thermal devices to reduce solar reflectance and enhance their transmittance (Ilenikhena, 2008).

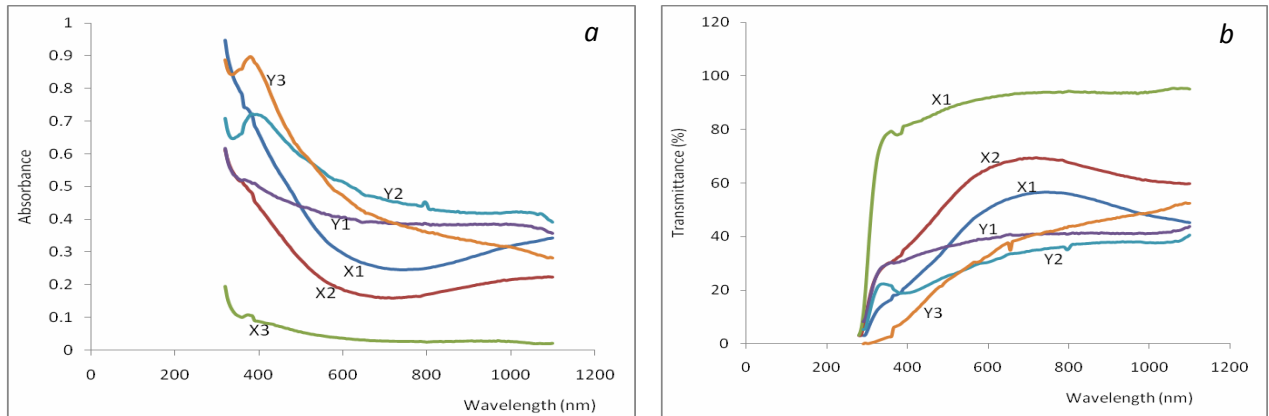


Figure 4: Plot of (a) absorbance and (b) transmittance against the incident photon's wavelength for the copper sulfide (X) and copper selenides (Y) thin films.

*Refractive index*

Study of the refractive index shows that the as-deposited copper selenide thin films has almost constant value (~2.6) at different photon energy though the value decreased slightly to about 1.7 with increasing photon energy for the annealed samples. However, two different trends of variations in refractive index were observed with respect to photons energy for the copper sulfide thin films. Figure 5 shows that the copper sulfide thin films annealed at 400°C has increasing trend from about 1.2 to 2.3 with increasing photons energy between 1.5eV and 4.0eV while the refractive index of the as-deposited and copper sulfide annealed at 100°C dropped from about 2.2 to 0.1 for the same range of photons energy.

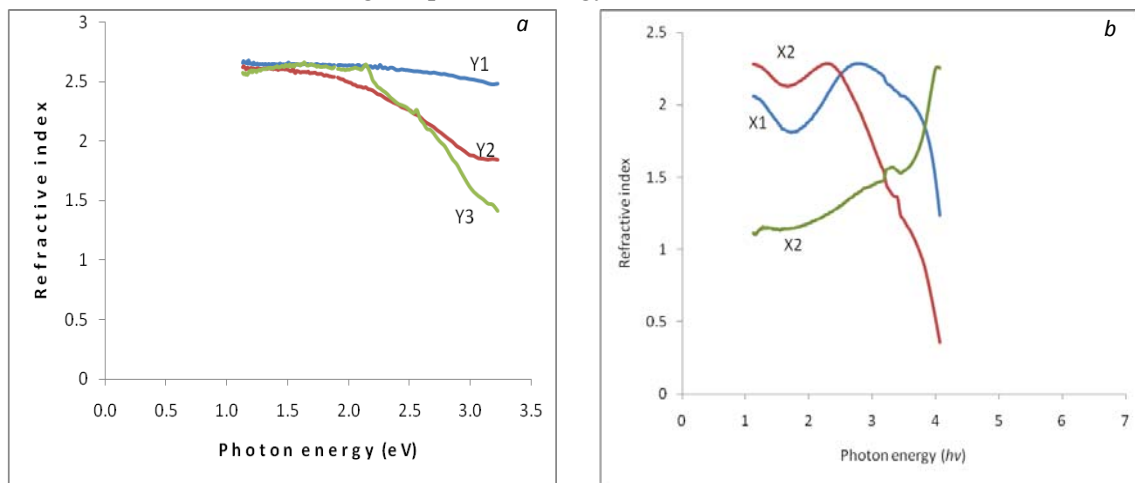


Figure 5: Refractive indices for the (a) copper sulfide (X) and (b) copper selenide thin films plotted against the photon energy.

*Optical conductivity*

Figure 6 displays the plot of the optical conductivity ( $\sigma_o$ ) against the photon energy ( $h\nu$ ). The values of the optical conductivity is related to the absorption coefficient ( $\alpha$ ), speed of light ( $c$ ) and the refractive index ( $n$ ) by the following expression (Pankove, 1971).

$$\sigma_o = \frac{\alpha nc}{4\pi} \quad (2)$$

The copper sulfide thin films have peak optical conductivity of about  $6.0 \times 10^{13} \text{S}^{-1}$  within the photon energy range 2.4eV - 3.6eV (visible region). Although the sample (X3) treated at higher

temperature (400°C) show very low conductivity at this range of the electromagnetic spectrum, a sharp increase (from 1.0 to  $6.0 \times 10^{13} \text{S}^{-1}$ ) in the optical conductivity was observed for photon energy between 3.4eV and 4.0eV (infra-red region). The optical conductivity of the copper selenide increased gradually from about  $5.0$  to  $7.5 \times 10^{13} \text{S}^{-1}$ . There was a peak conductivity value of  $22.5 \times 10^{13} \text{S}^{-1}$  for the copper selenide treated at 400°C at photon energy of 3.8eV.

## 5. Conclusion

Copper sulfide and copper selenide chalcogenide thin films were deposited successfully on glass substrates using the method of chemical bath technique. Structural studies show the presence of *chalcocite* ( $\text{Cu}_{1.96}\text{S}$ ) and *digenite* ( $\text{Cu}_9\text{S}_5$ ) phases with average grain size of 13.39nm for the  $\text{Cu}_x\text{S}$  thin films. Tetragonal  $\text{Cu}_3\text{Se}_2$  (*umangite*) and cubic  $\text{Cu}_2\text{Se}$  with average crystallite size of 35.79nm were observed for the  $\text{Cu}_y\text{Se}$  thin films. It was also observed that thermal treatment significantly improved the crystalline structure of the  $\text{Cu}_y\text{Se}$  in contrast to the copper sulfide thin films. The properties of the chalcogenide thin films show that they can possibly be used in solar energy conversions and in some opto-electronic devices.

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