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ANNEALING-INDUCED PHASE CHANGES AND VARIATIONS IN THE OPTICAL PROPERTIES OF CuS AND CuSe THIN FILMS SYNTHESIZED BY THE CBD TECHNIQUE

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Abstract— **An investigation has been carried out to determine the annealing-induced variation in the optical properties and possible phase changes that may occur in CBD synthesised CuS and CuSe thin films. Analytical techniques such as, Powder X-ray diffraction and optical absorption spectroscopy were used to characterize the films. The composition of the films and their phases were confirmed by Powder X-ray diffraction. Results showed that the as-deposited copper sulphide had several phases and after annealing in air, several copper sulphate phases were detected with copper sulphate pentahydrate being the dominant phase. The optical band gap of copper sulphide was 1.68 eV for the as-deposited sample and changed to 2.20 eV after annealing. Structural analysis of the copper selenide samples showed the presence of several phases in the as-deposited sample. After annealing, the diffraction pattern showed the presence of a single phase, krutaite with preferred orientation along the (111) plane. No diffraction peaks from other species could be detected in the annealed copper selenide sample, which seems to suggest that the obtained sample is pure The as-deposited copper selenide films possessed two band gaps of 1.20 and 1.33 eV which could be attributed to the presence of several phases. After annealing, the band gap changed to 2.20 eV. There was an increase in the average grain size of both the copper sulphide and copper selenide samples after annealing suggesting a further growth in grain size at this temperature.**

Index terms- **copper chalcogenide thin films, chemical bath deposition, phase change, annealing,**

I. INTRODUCTION

Transition metal chalcogenides: oxides, sulphides, selenides and tellurides are an important class of materials whose potential is increasingly being recognised due to a wide range of current and potential technological applications, in areas such as; solar energy conversion, solar control coatings, microelectronic devices, catalysts, sensors, optical filters and lasers [1,2]. Copper sulphide and copper selenide have been the focus of a significant number of investigations for these types of application.

Copper sulphide is an important group I-VI compound semiconducting material. It has chemical stability, a high absorbent coefficient, high refractive index, and transparency in the visible IR range [3]. It is also well known that these properties are strongly dependent on the method used for the deposition of the thin films [4].

At least five stable phases of the copper sulphide, Cu_xS ($1 \leq x \leq 2$), system are known to exist naturally. These phases are; covellite ($Cu_{1.00}S$), anilite ($Cu_{1.7}S$), digenite ($Cu_{1.80}S$), djurleite ($Cu_{1.97}S$), and chalcocite ($Cu_{2.00}S$) [5, 6]. Other phases that exist include yarrowite ($Cu_{1.12}S$) and spionkopite ($Cu_{1.14}S$) [7]. In nature, chalcocite and djurleite are physically difficult to distinguish from each other and are often found intermittently intertwined [6]. Their crystal structures are similar with both based on a monoclinic unit cell [6]. Mixed phases can also occur [8].

Copper selenide ($Cu_{2-x}Se$), has also generated a lot of interest in recent times because of its extensive use as a solar cell [9]. Copper selenide has colour ranging from blue-black to bluish green depending on the stoichiometric composition. The band gap of copper selenide is not well defined because of the wide variety of stoichiometric forms. [10] reported a direct and indirect band gap of 2.2 eV and 1.4 eV respectively, whilst [11] reported a band gap of 2.18 eV. Its indirect band gap is near the optimum value for solar cell applications and hence could offer a high efficiency conversion of up to 8.8 % [12]. Copper selenide is a semiconductor with p-type conductivity. The attraction of this material also lies in the feasibility of producing the ternary material, $CuInSe_2$ [13, 14] and also as an important surface impurity in Cu-rich $CuInSe_2$ [15]. Depending on the method of fabrication, copper selenide can exist in different crystallographic forms at room temperature, such as: cubic, tetragonal, orthorhombic or monoclinic forms [16, 17, 18, 19]. $Cu_{2-x}Se$ is known to have five stable phases; α- Cu_2Se (Bellidoite), Cu_3Se_2 (umangite), CuSe (Klockmannite), $CuSe_2$ (Krutaite), $Cu_{2-x}Se$ (berzelianite). The thermal stability of these compounds varies greatly depending on the composition. The various phases can, in some cases, be changed from one to another after deposition [8]. There are reports that CuSe has a hexagonal structure at room temperature and undergoes transition to an orthorhombic structure at 48 ^{0}C and back to a hexagonal structure at 120 ^{0}C [18, 20, 21].

These two compounds, CuS and CuSe, also have the advantage of being less toxic, compared to cadmium based compounds, abundant, and inexpensive.

Copper chalcogenides can be readily deposited by Chemical Bath Deposition. There is strong affinity between Cu and S or Se [8]. This strong affinity between elements is manifested as a low-solubility product of the various Cu chalcogenides [8]. A complicating factor in this deposition, however, is the large number of different phases and stoichiometries that can exist [8]. Inspite of this, CBD has several advantages over other techniques such as: reproducibility, nonhazardous and well suitable for large area deposition at relatively low temperatures [22, 23]. A variety of substrates such as insulators, semiconductors or metals can be used since these are low temperature processes which avoid oxidation and corrosion of substrate [24]. The CBD process generally operates under ambient conditions and has the potential to replace expensive energy and equipment intensive techniques.

Post deposition annealing of thin films can lead to significant changes in the structural, electrical, morphological and optical properties of semiconductor thin films [25] hence, it is a process worth studying.

In this paper, CuS and CuSe thin films have been deposited by the simple and cost effective CBD technique. The films are characterized by a variety of techniques to determine the phases present in the as-deposited sample and the possible phase changes that might occur as a result of annealing. The variation in optical properties due to annealing is also investigated.

II. METHODOLOGY

A. PREPARATION OF COPPER SELENIDE THIN FILMS

Copper chloride ($CuCl_2$) and Sodium selenosulphate were used as the source of Cu and Se ions respectively. The Sodium selenosulphate was prepared by the method described in [26]. All the chemicals used were of analytical grade. In a typical reaction, 5 ml of 1 M $CuCl_2$ solution, 10 ml of NH_3 and 5 ml of 1 M Na_2SeSO_3, were poured into a 100 ml beaker. 45 ml of de-ionized water was added to make up the final volume. The pH was measured and set to 12 by further dropwise addition of NH_3, which controls the pH of the solution and also functions as a complexing agent. The beaker was then placed in a water bath kept at a temperature of 80 °C (353K) and continuously stirred by a magnetic stirrer. The silica glass substrates were cleaned using a standard procedure and placed vertically inside the beaker to allow for CuSe film deposition. After 30 minutes, the coated substrates were taken out and washed with de-ionized water and any adherent particulate matter removed by ultrasonication. The deposited films were allowed to dry under ambient conditions before annealing and characterization. The films were annealed in air at 400 ^{0}C (673 K) for an hour.

The equation for the reaction process is given as:

$CuCl_2 + NH_3 \leftrightarrow Cu\ (NH_3)^{2+} + 2Cl^-$

$Na_2SeSO_3 + 2OH^- \leftrightarrow Se^{2+} + Na_2SO^4 + H_2O$

$Cu^{2+} + Se^{2-} \longrightarrow CuSe$

B. PREPARATION OF COPPER SULPHIDE THIN FILMS

The formation of copper sulphide from aqueous solution is well established, although the details of the solutions vary mostly in the choice of copper salt and/or sulphiding agent.

45 ml of de-ionized water was mixed with 5 ml of 1M $CuCl_2$ solution, 10-15 ml of NH_3 and 5 ml of 0.5 M CH_4N_2S (Thiourea) in a 100 ml beaker and pH set to 13. There was a colour change to deep blue when NH_3 was added. The beaker was then placed in a water bath kept at a temperature of 80 °C (353K) and continuously stirred by a magnetic stirrer. The cleaned silica glass substrate was placed vertically inside the beaker to allow for CuS film deposition. The deposition time and post-deposition processes are the same as those described for CuSe.

The as-deposited films appeared to be blue-black to the naked eye, and changed to black after annealing.

The equation for the reaction process is given as:

$CuCl_2 + NH_3 \leftrightarrow Cu\ (NH_3)^{2+} + 2Cl^-$

$(NH_2)_2SC + OH^- \leftrightarrow CH_2N_2 + HS^- + H_2O$

$HS^- + OH^- \longrightarrow S^{2-} + H_2O$

$Cu^{2+} + S^{2-} \longrightarrow CuS$

III. CHARACTERIZATION

The crystallographic structure of Cu_XS and $Cu_{2-X}Se$ thin films were analyzed with a PANalytical Empyrean series 2 Powder XRD with a Cu K_α radiation (1.54060 Å) source over the diffraction angle 2θ between 20 and 70 ^{o} and operating with an accelerating voltage and current of 45 kV and 40 mA respectively. The X-ray data were analyzed using the High score Plus software. The optical absorbance spectra of the thin films were obtained, using a UV mini Schimadzu UV-VIS spectrophotometer (model: UV mini-1240) within a wavelength range of 300 to 1100 nm at room temperature.

IV. RESULTS AND DISCUSSION

A. *Copper Sulphide (CuS)*

1) *X-Ray Diffraction*

Figure 4.1 shows the Powder X-ray diffraction pattern of the as-deposited copper sulphide thin film.

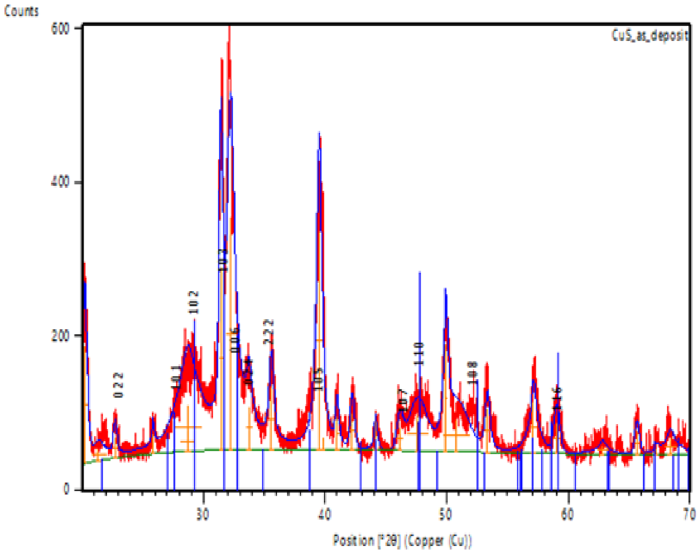

Fig. 4.1: XRD pattern of the as-deposited copper sulphide thin film

The spectrum in Fig. 4.1 shows several peaks confirming the polycrystalline nature of the sample. The peaks at 31.75, 32.14, 47.83, 29.21, 59.17, and 38.72^0 correspond to reflections from the (103), (006), (110), (102), (116), and (105) planes of the hexagonal covellite phase [COD 96-101-0956]. Other peaks were indexed to the copper sulphate (Brochantite) phase. The covellite phase had the highest score as shown in the summary of Table 4.1.

Table 4.1. Qualitative information on the relative amounts of different phases detected in the as-deposited thin film and their corresponding structure, analyzed by the High Score Plus software.

Visible Ref.Code	Chemical Formula	Score	Compound Name	Crystal System
96-101-0956	CuS	33	Covellite	Hexagonal
96-900-5584	$Cu_4SO_4(OH)_6$	23	Brochantite	Monoclinic

Similar observations on the presence of several phases in CBD copper sulphide have also been reported by [27]. The average grain size was calculated from the most intense peak, using the Scherrer formula which is given by.

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

Where D is the average grain size which was calculated as 6.49 nm.

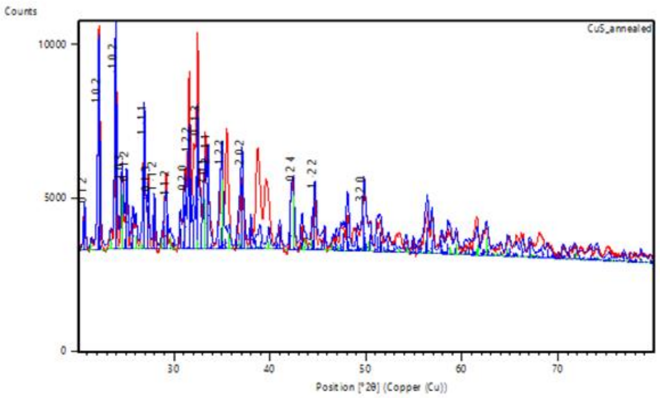

Fig. 4.2: XRD pattern of Copper sulphide powder annealed at 673 K

Fig. 4.2 is the XRD pattern of the copper sulphide sample annealed at 673 K. The sample contained a mixture of copper sulphate pentahydrate and Antlerite phases as shown in Table 4.2.

Table 4.2. Qualitative information on the relative amounts of different phases detected in the Copper sulphide thin film annealed at 673 K, and their corresponding structure, analyzed by the High Score Plus software.

Visible Ref.Code	Chem. Formula	Score	Compound Name	Cryst. Syst.
96-101-0528	$CuSO_4.5H_2O$	44	Copper sulphate pentahydrate	Anorthic
96-901-3963	$Cu_3(SO_4)(OH)_4$	41	Antlerite	Orthorhombic

From Table 4.2, it is clear that after annealing in air at 673 K, the copper sulphide was oxidized to form the copper sulphate. Copper sulphate pentahydrate had the highest score and is the dominant phase in the annealed sample. The peaks at 22.28, 23.93, 26.92, 31.59, and 32.46^0 correspond to reflections from the (102), ($\bar{1}02$), ($1\bar{1}1$), (122) and ($0\bar{1}3$) planes of the anorthic copper sulphate pentahydrate phase [COD 96-101-0528].

The average grain size was calculated using the Scherrer formula and found to be 40.00 nm. The increase in the grain size is in good agreement with [28], who also reported an increase in the average grain size after annealing at 673 K. According to [8], thin films annealed at temperatures above 573 K usually exhibited a large degree of crystal growth, and this might explain the increase in grain size observed.

A review of available literature indicates that the complexity of the copper sulphur system leads to mixed phase products during formation by many synthetic routes, including CBD. However, because many applications of copper sulphide require one specific phase, the synthesis of copper sulphide by CBD must be streamlined to produce the desired phase only and we are actively pursuing this.

4.1.2 Optical Absorption of copper sulphide

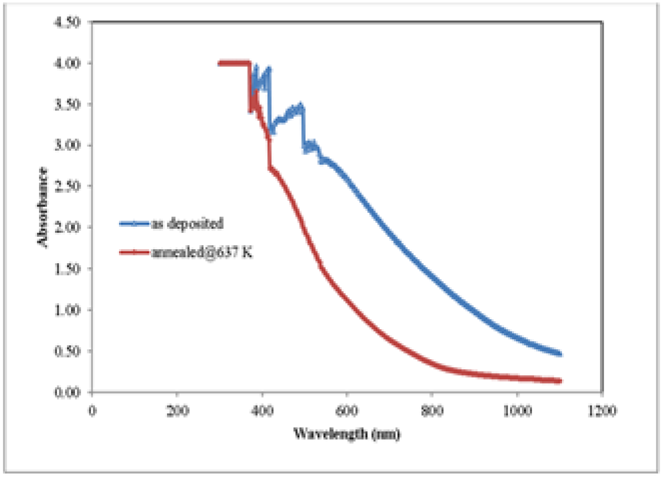

Fig. 4.3: A plot of Absorbance against Wavelength for as-deposited and annealed Copper sulphide thin film

Fig. 4.3 shows the absorption spectra of the as–deposited and annealed Cu_xS thin films. From the graph, the annealed film has lower absorbance values than the as-deposited film. Similar observation were made by [28] who reported that as-deposited Cu_xS thin films showed 90 % absorbance whiles films annealed at 473 K showed 50 % and films annealed at higher temperatures (573 K and 673 K) showed very low absorbance values (< 20 %). This decrease in absorbance after annealing may be attributed to minimizing structural imperfections in the annealed thin films resulting in a reduction in the density of defect states within the band gap. It can also be observed from the optical spectra that there is a shift in the fundamental absorption edge towards shorter wavelengths (blue shift) after annealing, suggesting an increase in band gap in the annealed sample

2) *Optical Band Gap of copper sulphide*

From the absorption spectra, the optical band gaps of the films were estimated using [29] relation for near edge absorption given as [30];

$$A = \frac{[K(h\nu - E_g]^{n/2}}{h\nu} \qquad 5.1$$

where υ is the frequency, h is the Planck‘s constant, *K* is a constant whiles *n* carries the value of either 1 or 4 for direct and indirect transitions respectively. Cu_xS is known to be a direct band gap semiconductor, thus n takes the value of 1. Fig. 4 shows $(Ah\nu)^2$ as a function of *hv.* The energy band gap is obtained by fitting a line to the linear portion of the graph and extrapolating the fitted line to the point where it intersects the *hv* axis [31] as shown in Fig. 4.4. The linear nature of the graph at high *hv* indicates the presence of a direct transition [31].

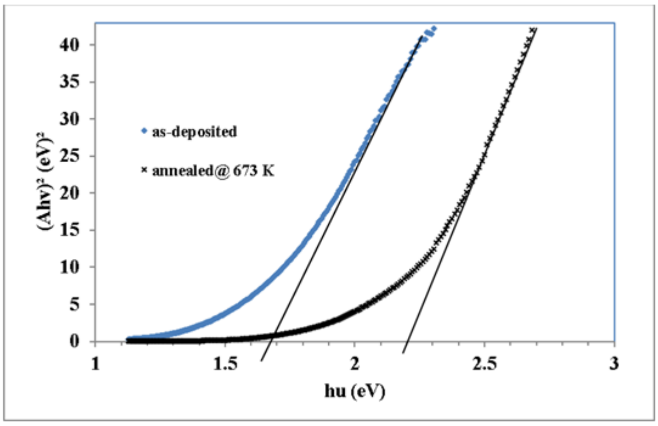

Fig. 4.4: A plot of $(Ah\nu)^2$ vs *hv* for as-deposited and annealed Cu_xS thin film

The optical band gap values were determined as; 1.68 eV for as- deposited and 2.20 eV after annealing at 673 K. These compare favorably well with values reported in literature [4, 32, 28, 33, 34].

B. COPPER SELENIDE

1) *X-RAY DIFFRACTION*

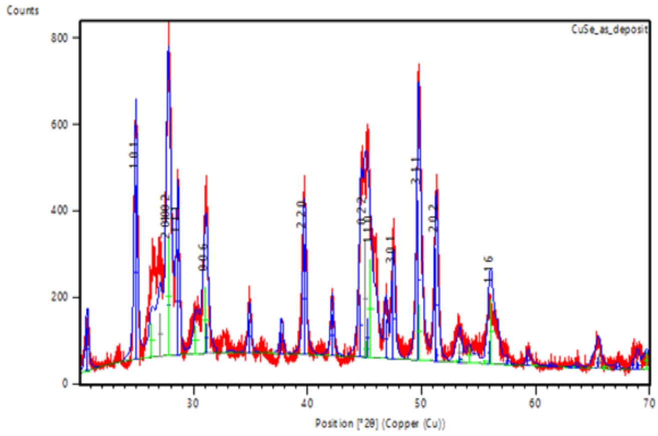

Fig. 4.5: XRD pattern of as-deposited Copper selenide thin film

Fig. 4.5 shows the XRD pattern of the as-deposited copper selenide thin film. The sample appears to be polycrystalline due to presence of several peaks in the XRD pattern. The pattern of prominent peaks suggests the formation of a heterogeneous phase of Cu_3Se_2, CuSe and $Cu_{2-x}Se$. The peaks are well matched well with the standard COD values (File no. 96-900-9857) for Cu_3Se_2, (File no. 96-900-0064) for CuSe and (File no. 96-900-8067) for $Cu_{2-x}Se$.

Qualitative analysis of the XRD results, show the Cu_3Se_2 (Umangite) phase has the highest score as seen in table 4.3, defining the dominant peaks. The peak at 24.96, 27.79, 27.78, 31.03, 44.63, 45.19, 49.68 and 51.24^0 correspond to reflections from the (101), (102), (006), (220), (310), (221), (311), and (202) planes of the tetragonal Umangite phase (File no. 96-900-9857), with preferred orientation along the (102) plane. A similar structure was reported by [35], but with a preferred orientation along the (006) plane of the hexagonal copper selenide structure. The average grain size, calculated using the Scherrer formula, was determined as 27.3 nm.

A careful observation of the grain sizes of the as-deposited CuS and CuSe films shows that CuSe forms larger grains. According to [8], studies on chemically deposited Cu-Se, showed that Cu-Se has a tendency to form relatively large crystals. He explained that this may be due to the high mobility of Cu^+ (although the tendency is much less for Cu-S) and the relatively low melting point of the Cu-Se compounds in general.

Table 4.3. Qualitative information on the relative amounts of different phases detected in the as-deposited copper selenide thin film, and their corresponding structure, given by the High Score Plus software.

Visible Ref.Code	Chem. Formula	Score	Compound Name	Cryst. Syst.
96-900-9857	Cu_3Se_2	63	Umangite	Tetragonal
96-900-0064	CuSe	40	Klockmannite	Hexagonal
96-900-8067	$Cu_{2-x}Se$.	41	Berzelianite	Cubic

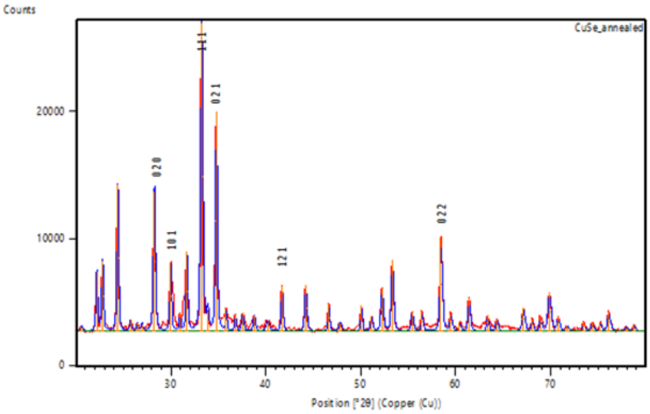

Fig. 4.6: XRD pattern of the Copper selenide thin film annealed at 673 K

Fig. 4.6 shows the XRD pattern of copper selenide thin film annealed at 673 K. The prominent peaks correspond to a single phase, the $CuSe_2$ (Krutaite) phase. Peaks at 33.29, 41.72 and 58.43^0 correspond to reflections from the (111), (121), and (022) planes of the orthorhombic krutaite phase (COD 96-410-5299). The preferred orientation is along the (111) plane. The sharp and well defined peaks indicate an improvement in crystallinity of the film after annealing. No diffraction peaks from other species could be detected, which seems to suggest that the obtained sample is pure [36]. This result is quite interesting.

The average grain size calculated using the Scherrer formula was found to be 41.6 nm suggesting an increase in grain size.

Table 4.4: Qualitative information on the relative amounts of different phases detected in the copper selenide thin film annealed at 673 K, and their corresponding structure, given by the High Score Plus software.

Visible Ref.Code	Chem. Formula	Score	Compound Name	Cryst. Syst.
96-410-5299	$CuSe_2$	13	Krutaite	Orthorhombic

C. Optical Absorption of copper selenide

Fig. 4.7 shows the optical absorption spectra of the as-deposited and annealed copper selenide thin films.

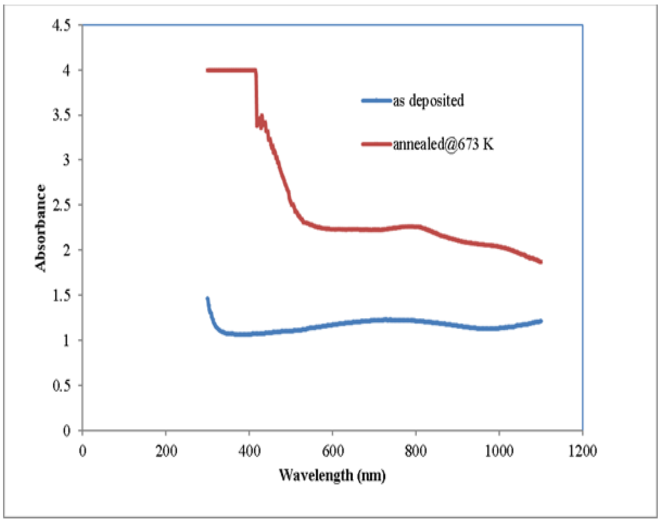

Fig. 4.7: A plot of Absorbance against Wavelength for as-deposited and annealed $Cu_{2-x}Se$ thin films

From Fig. 4.7 it is evident that there is a significant increase in absorbance after annealing at 673 K. Annealing at this temperature therefore produced a good absorber. The fundamental absorption edge shifted towards longer wavelengths (red shift) after annealing. These red shifts together with an increase in absorbance after annealing may be attributed to an increase in grain size which was confirmed by the XRD analysis. Similar observations on the absorbance of annealed CuSe thin films have been reported by [37]. The as-deposited films were blue-black and changed to bluish green after annealing. This color change is in agreement with a reported observation by [21], indicating a typical Cu_3Se_2 phase.

D. Optical Band Gap of copper selenide

Fig. 4.8 shows the band gap of as-deposited $Cu_{2-X}Se$ thin film, which was determined by the same procedure used for copper sulphide.

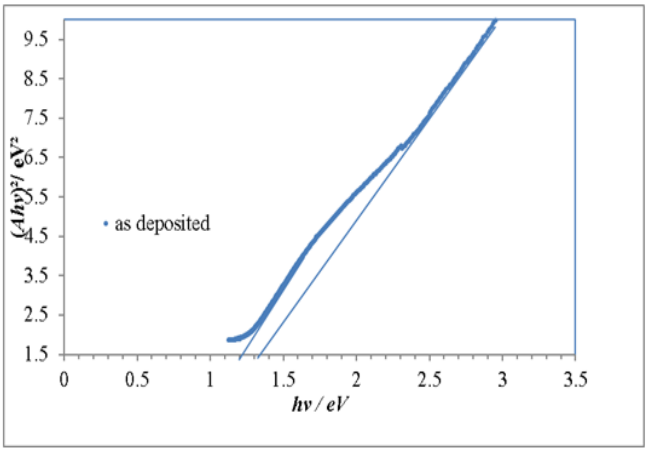

Fig. 4.8: A plot of $(Ah\nu)^2$ vs $h\nu$ for as-deposited $Cu_{2-X}Se$ thin film

From Fig. 4.8, extrapolations of the curves to the energy axis for zero absorption show the presence of two energy gaps; a lower one at 1.20 eV, and a higher one at 1.33 eV. These compare favourably well with values reported in literature [38, 39, 40, 41]. The presence of two band gaps in the as-deposited samples may be attributed to the heterogeneous nature (several phases) of the sample or possibly a defect state [42].

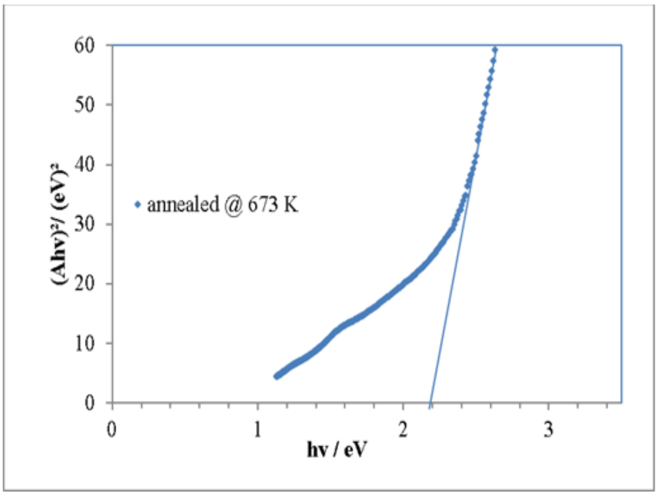

Fig. 4.9: A plot of $(Ahv)^2$ vs hv for CuSe thin film annealed at 673 K

From Fig. 4.9, films annealed at 673 K have only one band gap at 2.20 eV, suggesting the presence of a single phase. According to [38] the increase in band gap due to annealing may be understood by the improvement of crystallinity of the as-deposited film on annealing. This increase is also in agreement with reported observation by [43]. These observations together with the presence of a single phase are confirmed by the XRD analysis

V. CONCLUSIONS

Thin films of copper sulphide and copper selenide were successfully deposited by the chemical bath deposition technique. The as-deposited and annealed films were characterized by Optical Absorption Spectroscopy and Powder X-ray Diffraction.

Optical investigations showed thin films of copper sulphide had a band gap of 1.68 eV for the as-deposited samples and 2.20 eV after annealing. Structural analysis revealed the presence of several phases in the as-deposited sample with the covellite phase being dominant. After annealing, copper sulphate pentahydrate became the dominant phase.

The as-deposited copper selenide films possessed two band gaps of 1.20 and 1.33 eV which could be attributed to the presence of several phases. After annealing at 673 K, the band gap was 2.20 eV. Structural analysis of the copper selenide samples showed the presence of several phases. The dominant phase was the umangite phase with preferred orientation along the (102) plane. After annealing, the pattern of prominent peaks showed the presence of a single phase, krutaite with preferred orientation along the (111) plane. No diffraction peaks from other species could be detected, which seems to suggest that the obtained sample is pure.

There was an increase in the average grain size in the copper sulphide and copper selenide samples after annealing suggesting a further growth in grain size at this temperature.

From these results it is evident that annealing produced significant changes in the structural and optical properties of the copper sulphide and copper selenide thin films.

In addition, the similarities in the deposition conditions for both compounds open up the possibility of depositing ternary films of CuSSe.

VI. ACKNOWLEDGEMENT

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