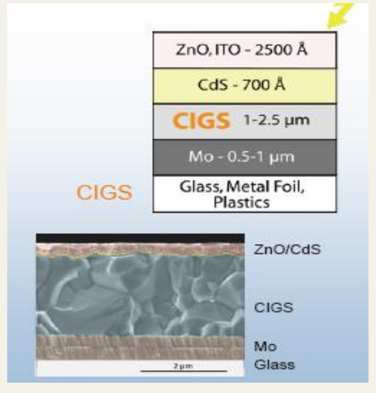
INVESTIGATION OF THE OPTICAL AND STRUCTURAL PROPERTIES OF CuS AND CuSe THIN FILMS DEPOSITED BY THE CHEMICAL BATH DEPOSITION TECHNIQUE

Bernice Y. Danu, F. K. Ampong, I. Nkrumah, R. K. Nkum, F. Boakye

Depart.ment of Physics, Kwame Nkrumah University of Science & Technology, Kumasi, Ghana

Introduction

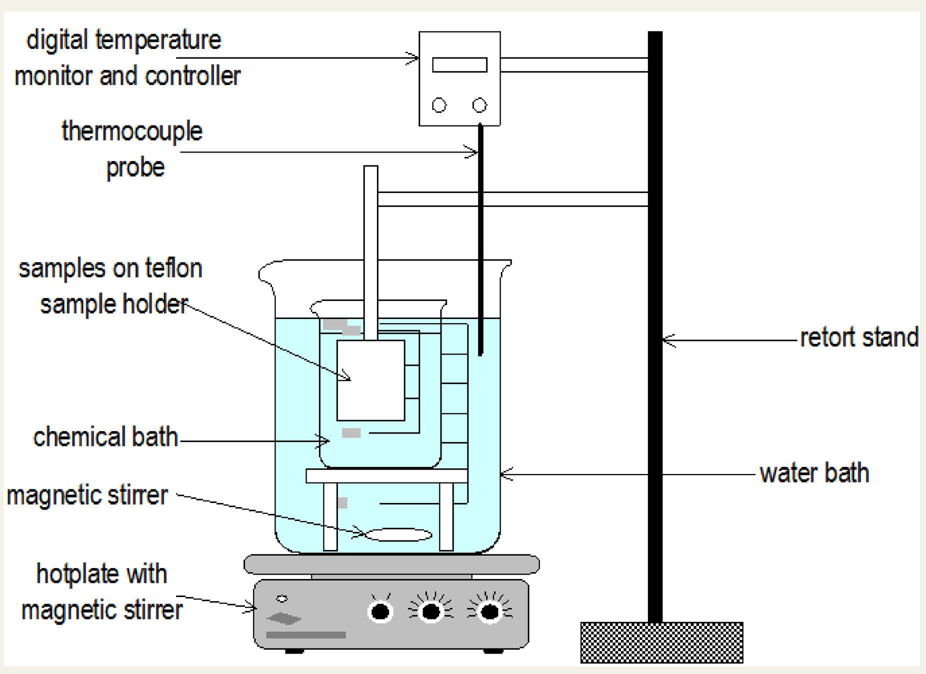
In recent times, copper sulphide (Cu_XS) and copper selenide ($Cu_{2-x}Se$) thin films have spurred up great interest due to their potential applications in the area of solar cells, optoelectronic devices, photoconductors, sensors, thin films polarizers, thermoelectric cooling materials and infrared detector devices. The attraction of these materials also lie in the feasibility of producing the ternary material, $CuInSe_2$ [1,2], and in combination with CdS to form Cu_2S/CdS [3] which are used as solar cell materials .



In Cu_XS, at least five stable phases of the copper sulphide system are naturally known to exist depending on the stoichiometric composition ($1 \leq x \geq 2$). $Cu_{2-x}Se$ on the other hand, also exists in five stable phases depending on the stoichiometric composition. Due to the variable wide band gap of these materials, they can be used as window layer materials in solar cell applications.In view of this, more attention is being given in producing good quality (Cu_XS, $Cu_{2-x}Se$) thin films for comprehensive optical studies and their various applications

The Technique

The CBD process involves the deposition of a thin film on a substrate from a reaction occurring in solution. The process requires the substrate to be immersed in a supersaturated solution of aqueous precursors such as metal salts, complexing agents, and pH buffers. This technique possesses many advantages over the others such as its non-sophisticated instrumentation, convenience for large area deposition, applicable to a wide range of substrates, and generally very simple .Chemical bath deposition is becoming an important deposition technique for thin films of compound materials like chalcogenides[4]



Materials used:

Copper sulphide

1. **$CuCl_2$: 99% purity from Sigma Aldrich**
2. **Thiourea: 98% purity from Sigma Aldrich**
3. **Ammonia: 99% purity from Sigma Aldrich**

Copper selenide

1. **$CuCl_2$: 99% purity from Sigma Aldrich**
2. **Sodium selenosulphate: 99+% purity from Sigma Aldrich**
3. **Ammonia: 99% purity from Sigma Aldrich**

Experimental Methods

Copper sulphide

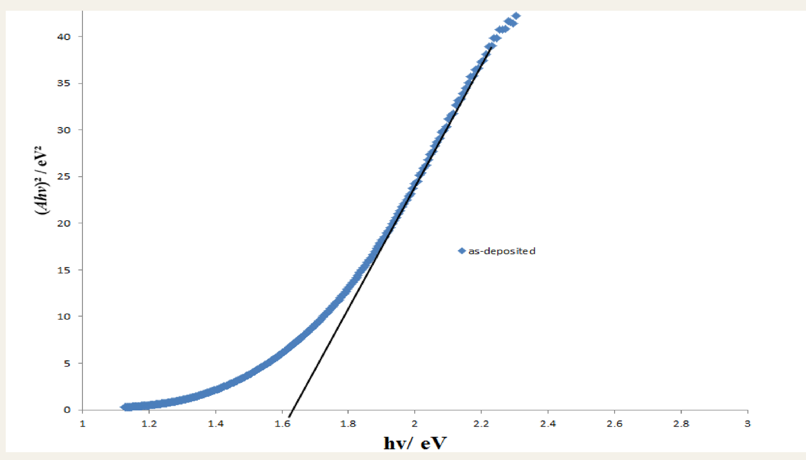
- $CuCl_2$ (1M) , CH_4N_2S (0.5 M)& 10-15 ml of NH_3
- Deposition Temperature & Time – 80°C & 30mins
- pH ~ 13

Copper selenide

- $CuCl_2$ (1M) , Na_2SeSO_3 (1 M) & 10 ml of NH_3
- Deposition Temperature & Time – 80°C & 30mins
- pH ~ 12

- Glass substrates introduced right after mixing all reagents
- After deposition, the substrates were allowed to dry under ambient conditions before film characterization or a further annealing step.

RESULTS – Optical Band Gap of Copper sulphide

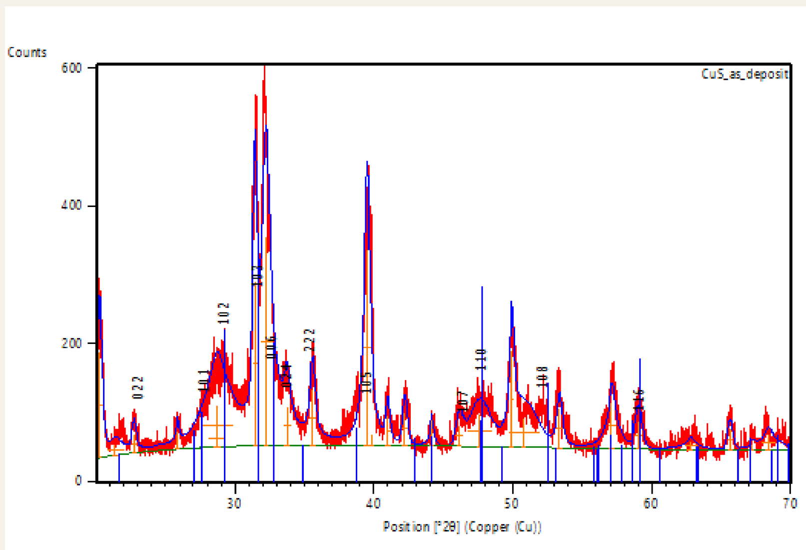


Band gap of as-deposited Cu_XS thin film

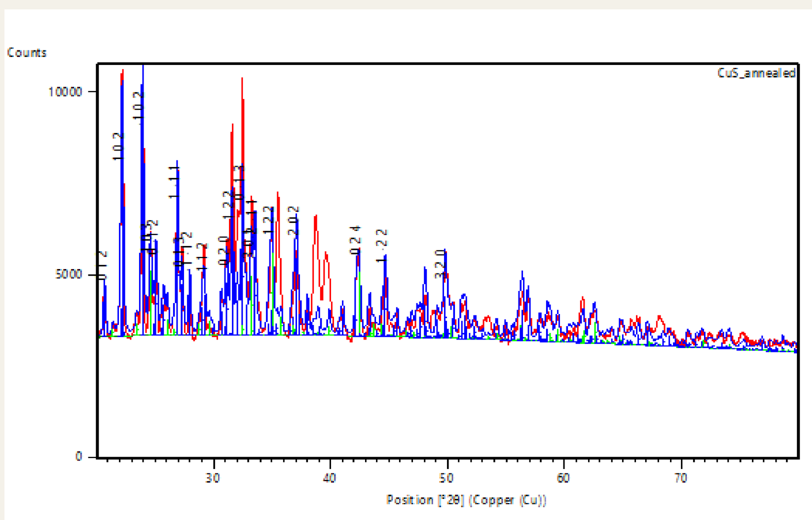
Table 1: Summary of band gap values of copper sulphide thin films

Temperature/ ° C	Band gap/ eV
As- deposited	1.6
Annealed at 300° C	2.2
Annealed at 400° C	2.2

POWDER X-RAY DIFFRACTION ANALYSIS OF Cu_xS



X-ray difraction pattern of as-deposited Cu_XS



X-ray diffraction pattern of annealed Cu_XS

X-ray diffraction measurements of copper sulphide showed several phases with a dominant phase of covellite in the as-deposited sample. After annealing at 400°C, the dominant phase was copper sulphate pentahydrate. The preferred orientation was along the (103) plane in the as-deposited sample and the preferred orientation after annealing was along the ($\bar{1}02$) plane.

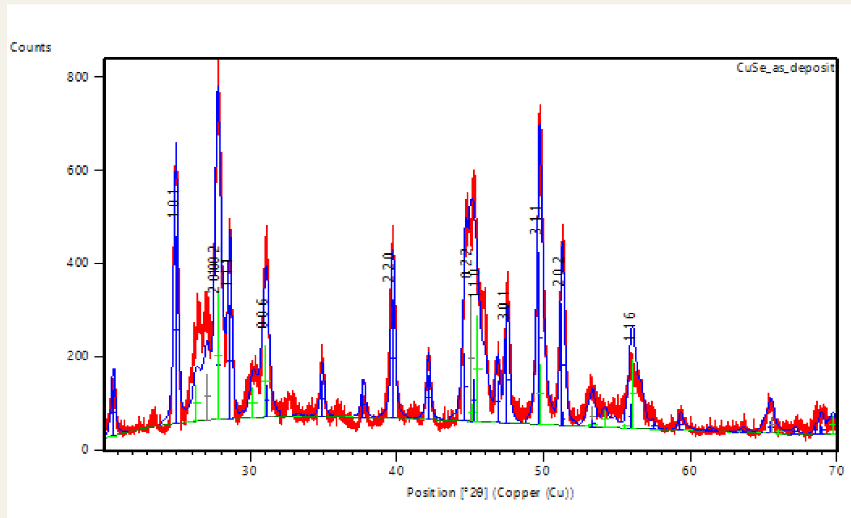
Reference

3. **Rothwarf, A. and Barnett, A. M., (1977)**, *IEEE T. Electron De*, 24, 381
4. **McPeak M. P. (2010).** Chemical Bath Deposition of Semiconductor Thin Films & Nanostructures in Novel Microreactors, PhD Thesis, Drexel University, p1

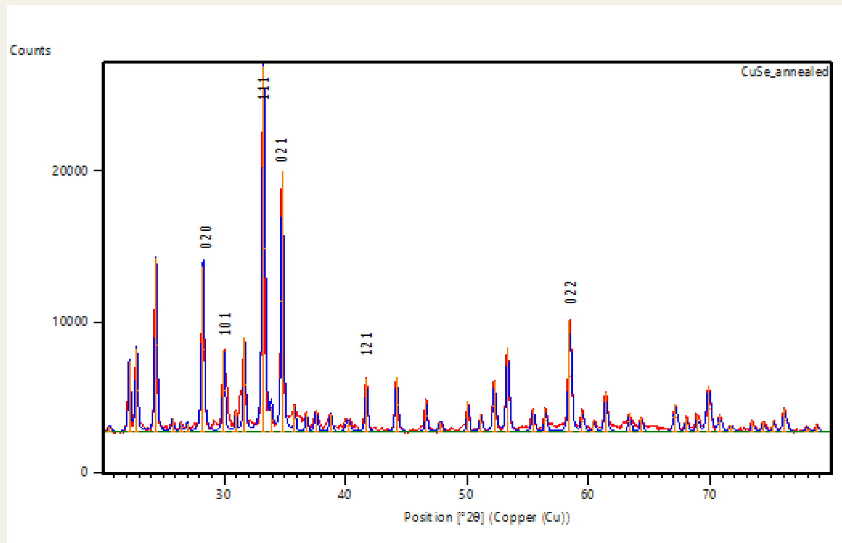
Summary of band gap values of copper selenide thin films

Temperature/ °C	Band gap/ eV
As- deposited	1.2 and 1.4
Annealed at 200°C	1.0 and 1.2
Annealed at 300°C	2.2
Annealed at 400°C	2.2

X-ray diffraction pattern of $Cu_{2-x}Se$



X-ray diffraction pattern of as- deposited $Cu_{2-x}Se$



X-ray diffraction pattern of annealed $Cu_{2-x}Se$

In copper selenide , the dominant phase was umangite and after annealing at 400°C, the dominant phase was krutaite. The preferred orientation in the as-deposited sample was along the (101) plane and after annealing, it had a prefered orientation along the (111) plane.

Conclusion

1. Copper sulphide and Copper selenide thin films with the required composition were successfully deposited by the chemical bath deposition technique .
2. The band gaps of copper sulphide ccalculated from optical absorption spectroscopy,were found to be 1.6 eV for the as-deposited samples and 2.2 eV after annealing, whilst copper selenide had a band gap of 1.2 and 1.4 eV for the as- deposited sample and 2.2 eV after annealing. The presence of two band gaps in the as-deposited sample may be attributed to the presence of more than one phase.
3. X-ray diffraction analysis of the powder samples of copper sulphide showed a dominant phase of covellite with a preferred orientation along the (103) plane for the as-deposited sample and a dominant copper sulphate pentahydrate phase after annealing. The preferred orientation was along ($\bar{1}02$) plane. The average grain size, determined using the Scherrer formular increased from 1.0 nm for the as-deposited sample, to 6.4 nm after annealing.
4. X-ray diffraction measurements of the powder samples of copper selenide showed a dominant phase of umangite with a prefered orientation along the (101) plane. Annealing the sample showed a dominant phase of krutaite with a preferred orientation along the (111) plane. There was an increase in grain size from 4.4 nm to 5.6 nm after annealing.

Reference

1.Chu T.L, Chu S.S, Lin S C S C and Yue J J, (1984), Quoted by R H Bari, V. Ganesan, S. Potadar and L .A. Patil, Structural, optical and electrical properties of chemically deposited copper selenide films, *Bull. Mater. Sci*., Vol. 32, No. 1, 2009, pp. 37–42.
2.O'Brien R N and Santhanam K S V, (1992), Quoted by R H Bari, V Ganesan, S Potadar and L A Patil, Structural, optical and electrical properties of chemically deposited copper selenide films, *Bull. Mater. Sci*., Vol. 32, No.1, 2009, pp. 37–42

Contact Information: Bernice Yram Danu, Tel: 0233 (0) 249 289361 (GH),