

# Crystallographic and Micrographic Structure of Copper Indium Gallium diSelenide (CIGS) Semiconductor Thin Films using Chemical Bath Deposition (CBD) Technique

Q. A. Adeniji<sup>1</sup>, Kola Odunaike<sup>2</sup>

<sup>1,2</sup>Department of Physics, Olabisi Onabanjo University, Ago-Iwoye, Nigeria

**Abstract:** CIGS semiconductor thin films have been deposited successfully on microscopic glass substrates using Chemical Bath Deposition (CBD) technique at 85°C. The mixture for the CIGS baths were prepared by mixing 10ml of 0.3 M of CuCl<sub>2</sub>.H<sub>2</sub>O and 5ml of TEA in a 50ml beaker, 10ml of 0.2 M of InCl<sub>3</sub>.4H<sub>2</sub>O, 10ml of 0.4 M of GaCl<sub>3</sub> complexed with 5 ml of 0.5M EDTA in a 100 ml beaker and this step was repeated for 0.6 M and 0.8 M of GaCl<sub>3</sub> for 1:2, 1:3 and 1:4 In:Ga ion concentrations ratio respectively. The crystallographic (structural) and morphological (micrographic) properties of the as-deposited and annealed CIGS films at 450°C temperature have been studied with aid of X-ray diffractometer and Scanning Electron Micrograph (SEM) machine respectively. The compositional and chemical analyses of the films were determined using X-ray Fluorescent (XRF) spectroscopy (Sky Ray Explorer). The crystalline nature of the CIGS (both 1:2 and 1:3) thin films were established, indicating that the as-deposited films were amorphous in nature whereas their respective annealed films were crystalline in nature which showed the effect of annealing on the samples. The XRF analysis confirmed the presence of CIGS and other elements in the deposited films. The SEM micrograph of the CIGS (1:2) thin films showed a coarse distributed structure and finely distributed structure for as-deposited and annealed films respectively but as-deposited CIGS (1:3) showed isolated spongy spots and pinholes while its annealed film showed reduced pinholes and relatively fine structural outlook.

**Keywords:** CIGS, Thin films, Crystallographic, Micrographic Structure, CBD technique

## 1. Introduction

The most common chalcopyrite used for solar cells is a mixture copper indium diselenide (CuInSe<sub>2</sub>, CIS) and copper gallium diselenide (CuGaSe<sub>2</sub>, CGS). This mixture is called copper indium gallium diselenide (Cu (In<sub>x</sub>Ga<sub>1-x</sub>)Se<sub>2</sub>, CIGS), where the x can vary between 0 and 1. Several research groups and companies use a compound that also contains sulfur; it is called copper indium gallium diselenide/disulfide (Cu (In<sub>x</sub>Ga<sub>1-x</sub>) (Se<sub>y</sub>S<sub>1-y</sub>)<sub>2</sub>, CIGSS), where y is a number in between 0 and 1. The physical properties of CIGS (S) are rather complex and many different views exists on these properties among scientists.

Group I-III-VI<sub>2</sub> family of semiconducting compounds appear to be a promising candidate for use in optoelectronic devices, there are some members of this family, such as CIGS for which the information concerning the optoelectrical properties is not common (Shay and Wernick, 1975). Moreover, these properties are highly dependent on their structure and composition which in turn are strongly related to the film growth parameters. A number of deposition techniques have been used in order to produce thin films of these materials. Solution-processed CIGS thin film has a porous nature, which has resulted in inefficient solar cell performance (Uhl *et al.*, 2011). However, in the aspect of light transmission, the porous morphology of the film can be favourable (Ding *et al.*, 2013).

The use of CIGS materials in device technology could motivate a frame work for the study of many research problems. Extensive basic and applied research on CIGS

both in thin film and single crystal form, have shown a considerable and measurable potential for success. More so, there is a need for further studies in order to have a better understanding of the fundamental properties. In light of this, two CIGS films with different levels of In:Ga ion concentration were prepared by chemical bath deposition technique to investigate the crystallographic and micrographic structure of the film.

## 2. Experimental Details

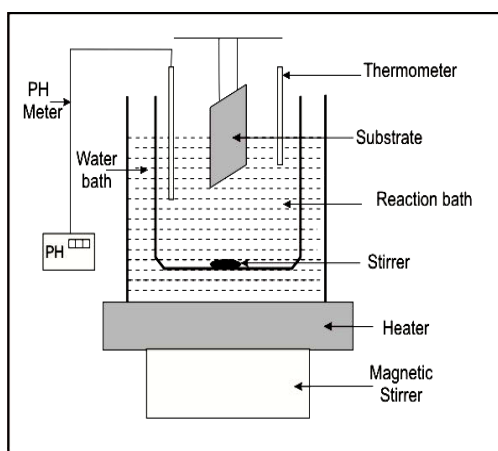
The precursors used in this investigation were copper (II) chloride dihydrate (CuCl<sub>2</sub>.H<sub>2</sub>O) as the source of Cu<sup>2+</sup> and Triethanolamine (TEA) as a complexing agent, sodiumselenophite (Na<sub>2</sub>SeSO<sub>3</sub>) as a source of selenium ion (Se<sup>2-</sup>) and Indium (III)chloride tetrahydrate (InCl<sub>3</sub>.4H<sub>2</sub>O) as a source of indium ion (In<sup>3+</sup>) and Gallium trichloride (GaCl<sub>3</sub>) was used as the source for Gallium ion (Ga<sup>3+</sup>) whereas Ethylene Ditetra amine acid (EDTA) as a complexing agent for In<sup>2+</sup> in the reaction mixture of both. Ammonia (NH<sub>3</sub>) was used to adjust the pH of the solution. The sodium selenosulphite was prepared by refluxing 9.0 g of selenium power with approximately 15.0g of anhydrous sodium sulphite (Na<sub>2</sub>SO<sub>3</sub>) in 200ml of distilled water for 6 hours at 80°C thereby making 0.2 M of Na<sub>2</sub>SeSO<sub>3</sub>.

CIGS thin films were deposited on glass substrates by CBD technique at 85°C. Prior to the deposition, the glass substrates were degreased in HCl for 24 hours, washed with detergent, rinsed with distilled water and dried in air. The mixture for the CIGS baths were prepared by mixing 10mls of 0.3 mol of CuCl<sub>2</sub>.H<sub>2</sub>O and 5mls of TEA in a

50mls beaker, 10mls of 0.2 mol of  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ , 10mls of 0.4 M of  $\text{GaCl}_3$  complexed with 5 mls of 0.5M EDTA in a 100mls beaker, this step was repeated for 0.6 M and 0.8 M of  $\text{GaCl}_3$  for 1:2, 1:3 and 1:4  $\text{In}^{3+} : \text{Ga}^{3+}$  concentration ratio respectively. The pH of the solution of each bath was adjusted by addition of  $\text{NH}_3(\text{aq})$ . After which 10 mls of  $\text{Na}_2\text{SeSO}_3$  and some distilled water was added to obtain a final volume of 100mls. The reaction mixture was initially stirred and maintained a temperature of  $85^\circ\text{C}$  for deposition. Four cleaned glass substrates were vertically immersed into the chemical baths with the help of synthetic foam. The deposition process was carried out at room temperature and 9 hours in order to determine the optimum condition for the deposition of CIGS. Thin films allowed to dry under ambient condition, one of the samples labeled as-deposited and the other annealed at  $450^\circ\text{C}$  for each In:Ga ion concentration ratio. The various deposition temperatures and the pH (11.5-11.3) were monitored with Mettler Toledo AG 8603 pH meter. The substrates were removed, dried in open air at room temperature and kept. Table 1 shows the chemical bath compositions while Figure 1 shows the schematic experimental set-up for the deposition of the thin films.

**Table 1:** Chemical Bath Compositions for the deposition of CIGS Thin films

Baths (In:Ga)	Cu	In	Ga	Se	pH
	Concentration (M)				
S <sub>1:2</sub>	0.3	0.2	0.4	0.2	10.13
S <sub>1:3</sub>	0.3	0.2	0.6	0.2	10.84

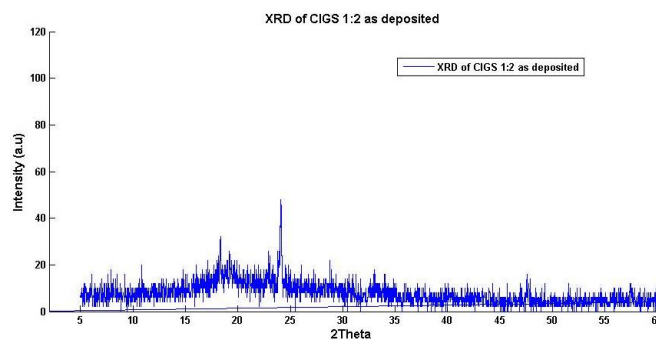


**Figure 1:** Schematic experimental set-up for Chemical Bath Deposition of CIGS

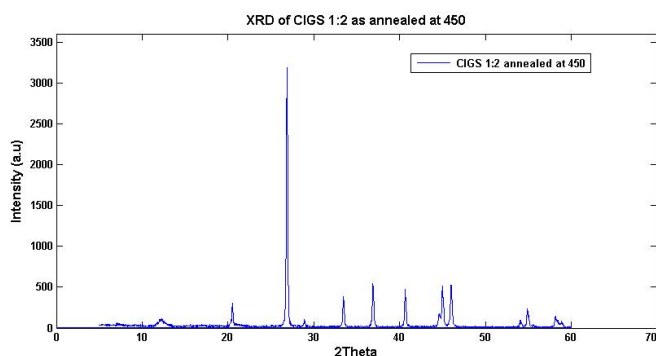
### 3. Results and Discussion

#### 3.1 Results

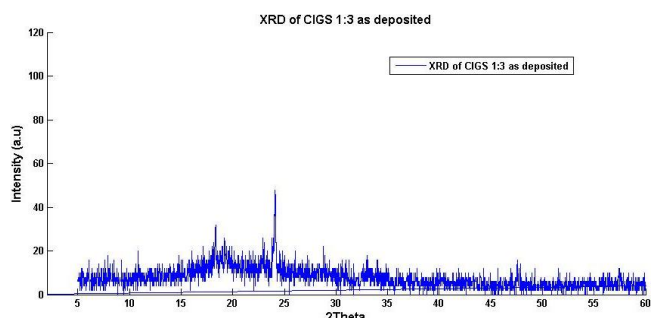
The crystallographic structure of CIGS was analyzed with an X-ray diffractometer. Scanning Electron Micrograph (SEM) measurements were conducted using SEM machine (Inspect X50). The thickness, composition of layers and coating and chemical composition analysis of the thin films were determined using X-ray Fluorescent (XRF) spectroscopy (Sky Ray Explorer). The Structural analysis of the CIGS thin films was done by XRD machine (Shimadzu 6000).



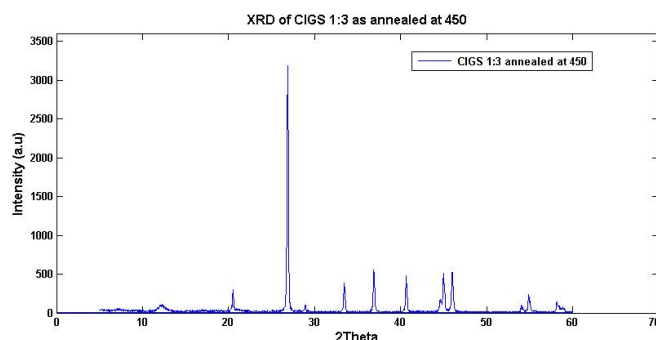
**Figure 2:** XRD Spectra of CIGS (1:2) as deposited



**Figure 3:** XRD Spectra of CIGS (1:2) annealed at  $450^\circ\text{C}$



**Figure 4:** XRD Spectra of CIGS (1:3) as deposited



**Figure 5:** XRD Spectra of CIGS (1:3) annealed at  $450^\circ\text{C}$

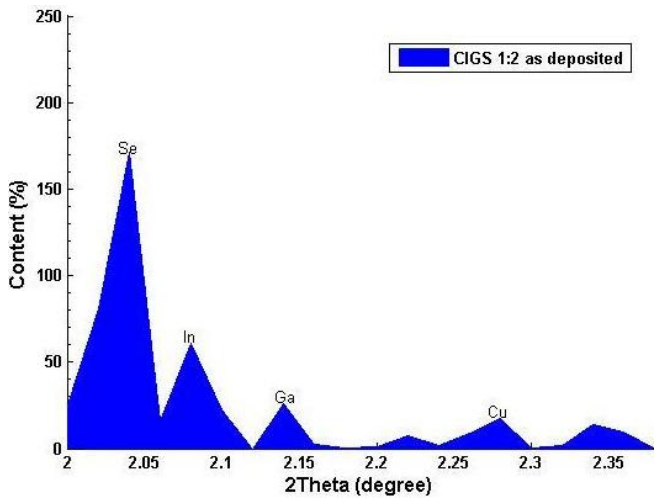


Figure 6: XRF spectra for CIGS (1:2) as deposited

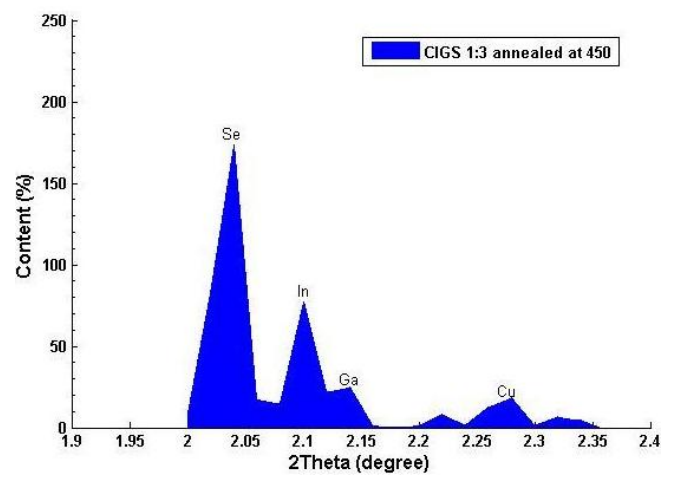


Figure 9: XRF spectra for CIGS (1:3) annealed

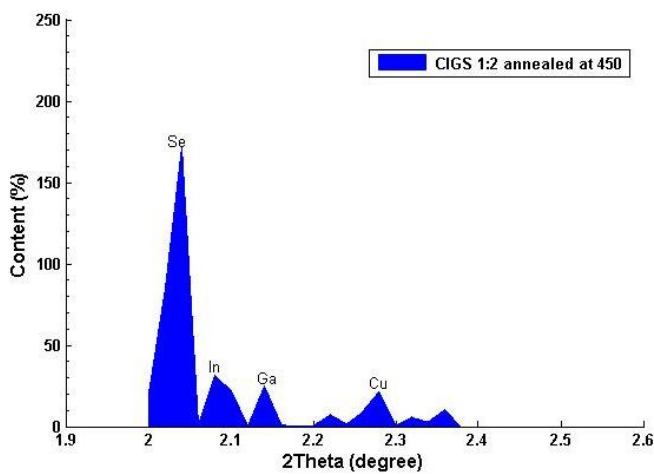


Figure 7: XRF spectra (1:2) for CIGS annealed

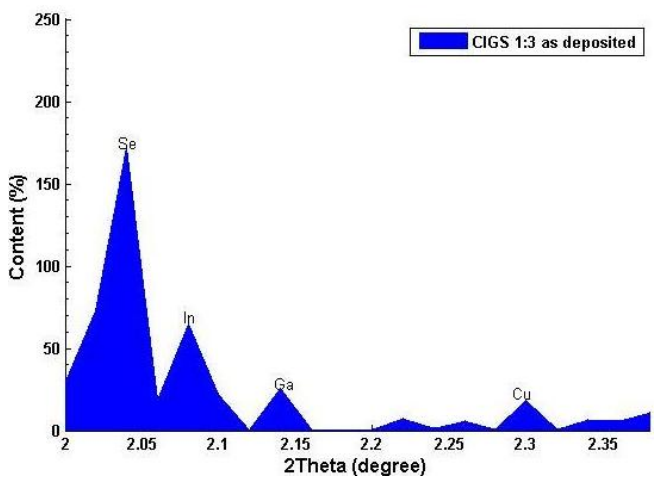


Figure 8: XRF spectra for CIGS (1:3) as deposited

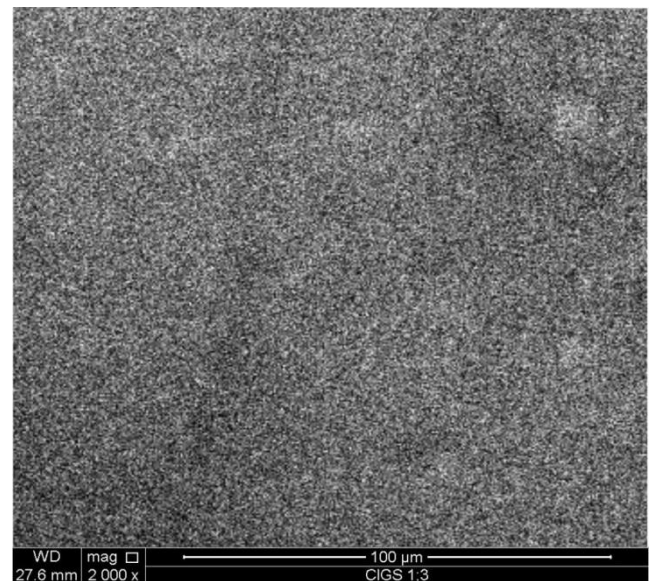
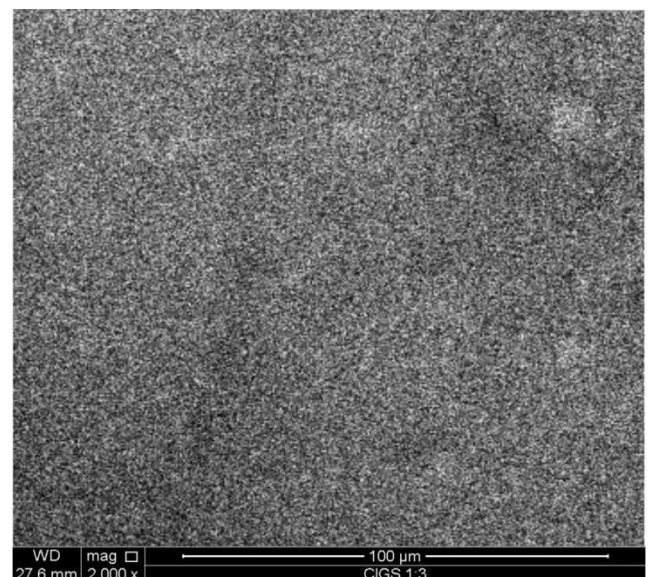


Figure 9: XRF spectra for CIGS (1:3) annealed



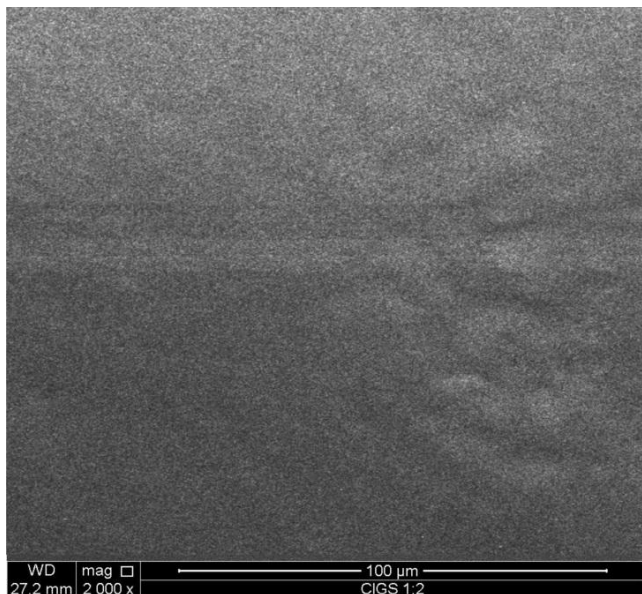


Figure 11: SEM image for CIGS (1:2) annealed

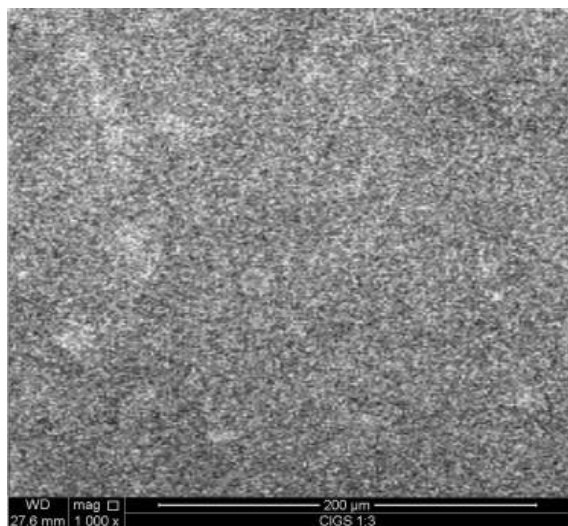


Figure 12: SEM image for CIGS (1:3) as deposited

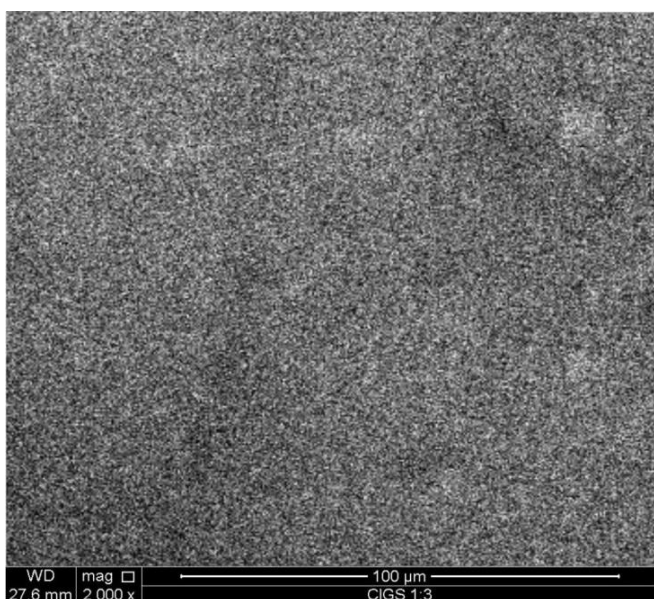


Figure 13: SEM image for CIGS (1:3) annealed

#### 4. Discussion

Figures 2-5 shows the XRD patterns for the as-deposited and annealed CIGS thin films of thickness 0.2 nm. The XRD patterns revealed amorphous nature of the films with a broad band at indistinct diffraction peaks. This amorphous structure was found to be unstable as thermal annealing subsequently leads to crystallization in the film (Fang *et al.*, 2001). The thermal annealing of the as-deposited thin films at 450°C for 180 minutes resulted to crystallization with distinct peaks. This indicates that at this temperature, the crystallites in the samples have been re-ordered thereby improving the crystallinity of the materials. In this way, the films become free of probable defects generated during the deposition. In particular, the FWHM for the samples decreases with increase in gallium concentration of In: Ga ratio. This indicates that CIGS (1:2) was the optimum concentration. A similar result was reported by Venkatachalam *et al.* (2008). The X-ray diffraction (XRD) spectra of CIGS are shown in Figures 2 and 3 for 1:2 and Figures 4 and 5 for 1:3 In to Ga content respectively. The structure of the 1:2 films shows a peak at intensity count of 24 with  $24.08^\circ 2\theta$  for the as deposited and 0.3966 FWHM whereas it was 2148 intensity count with  $26.91^\circ 2\theta$  and 0.4923 FWHM for the annealed (450°C). The structure of the 1:3 films shows a peak at intensity count of 32 with  $24.07^\circ 2\theta$  for the as deposited and 0.3446 FWHM whereas it was also 2148 intensity count with  $26.91^\circ 2\theta$  and 0.4923 FWHM for the annealed (450°C). It is somewhat difficult to say anything about the existence of the chalcopyrite structure because in strongly oriented films identification of the characteristic chalcopyrite peaks is difficult due to the sensitivity limits of the XRD technique. After annealing process, the CIGS thin films exhibited similar diffraction peak around  $26.9^\circ$ . And this is in agreement with the work of Chihi *et al.* (2016). The Full Width at High Maximum (FWHM) decreases with increase in concentration of In:Ga ratio. This effect reveals that with increase in concentration, the deposited CIGS alloys are better.

Figures 6-9 show the weight percent composition (measurement accuracy of  $\pm 2\%$ ) for a range of total weight of deposit for different samples of CIGS thin films. The apparent measurement error could be due to the fact that the sample area for analysis was restricted and the calibration conditions and those of the analyses were not identical. Energy dispersive X-ray fluorescence analysis confirmed the presence of Cu (4.4%), In (37.4%) and Se (50.6%), with  $2.30^\circ$ ,  $2.05^\circ$  and  $2.10^\circ$  of  $2\theta$  values respectively, which shows that the CIS deposited is nearly stoichiometry. Also, Cu (6.3%), In (19.1%), Ga (9.5%) and Se (55.6%), with  $2.30^\circ$ ,  $2.10^\circ$ ,  $2.15^\circ$  and  $2.05^\circ$  of  $2\theta$  values show that the CIGS deposited is stoichiometry (1:2). Similar results were obtained from CIGS (1:3)-Cu (5.3%), In (23.1%), Ga (7.1%) and Se (62.1%), suggesting the ratio 1:2 has the optimized concentration. This is consistent with the work of Padam, (1987). The gallium and copper contents are very consistent and close to the theoretical values of 5.33 wt.% and 1956 wt% respectively. These results were not in agreement with the work of Ahmed (1995) who deposited the films using flash evaporation method. The results from XRF indicated that the as-grown films were slightly deficient in selenium and complete absence of copper was found in films

deposited at source temperatures below 1100 °C. These results make chemical bath deposition (CBD) more preferable to other methods for its large areas of coating thereby revealing sufficiently the elemental compositions in the deposited films.

The scanning electron micrographs of the CIGS samples prepared under optimized deposition conditions are shown in Figures 10 - 13. It can be seen that the grains in the SEM micrograph of the CIGS samples are alike and distributed uniformly over a smooth homogenous background without visible defects such as cracks, peeling or pinholes. The grain size of the as-deposited samples were estimated from the SEM micrographs and were found to be 200µm whereas 100µm grain size was observed for the annealed samples with magnification of 500. This agrees with the report of Babatunde (2017) who deposited ZnSe on SLG using thermal evaporation technique. By considering the deposition conditions, it can be concluded that the in-situ annealing resulted in a more relaxed and denser structure. No clear difference between the films as deposited and annealed at 450 °C temperature. This is similar to the report of Sampathkumar *et al.* (2013).

## 5. Summary

CIGS semiconducting thin films have been successfully deposited on glass substrates by Chemical Bath Deposition (CBD) technique. The structural, compositional and morphological properties of the as-deposited and annealed thin films at 450 °C temperature have been investigated. The crystalline nature of the CIGS (both 1:2 and 1:3) films were established, indicating that the as-deposited films were amorphous in nature whereas their respective annealed films were crystalline in nature which showed the effect of annealing on the samples. The XRF analysis confirmed the presence of CIGS and other elements in the deposited thin films. The SEM micrograph of the CIGS (1:2) thin films showed a coarse distributed structure and finely distributed structure for as-deposited and annealed films respectively but as-deposited CIGS (1:3) showed isolated spongy spots and pinholes when its annealed film showed reduced pinholes and relatively fine structural outlook.

## References

- [1] Ahmed, E. (1995). Growth and Characterization of Cu (In,Ga)Se, Thin Films for Solar Cell Applications. Ph.D Thesis, University of Salford, U. K.
- [2] Babatunde, R. A. (2017). Synthesis and Characterization of ZnTe and ZnSe Thin films as window layers for heterojunction solar cell deposited by thermal vacuum evaporation. M.Sc. Dissertation, Olabisi Onabanjo University, Ago-Iwoye. Nigeria.
- [3] Chihi, A., Boujmil M. F. and Bessais, B. (2016). Optical and electrical characterization of CIGS thin films grown by electrodeposition route. Journal of Materials Science & Processing. DOI 10.1007/s00339-016-9603-z.
- [4] Fang, G., Liu, Z. and Yao, K. L. (2001). Fabrication and characterization of electrochromic nanocrystalline WO<sub>3</sub>/Si (111) thin films for infrared emittance modulation applications. Journal of Physics D: Applied Physics, Volume 34, Number 15.
- [5] Padam, G.K. (1987). Composition and structure of chemically deposited CuInSe<sub>2</sub> thin films. Mat. Res. Bull. Vol. 22, Issue 6, Pp. 789-794
- [6] Sampathkumar, W. I. (2013). Characterization of Randomly rough Surfaces in Nanometric scale using Methods of Modern Metrology. A Ph.D Thesis of Masaryk University, Brno, Czech Republic.
- [7] Venkatachalam, M., Kannan, M.D., Jayakumar, S., Balasundaraprabhu, R., Nandakumar, A.K. and Muthukumarasamy N. (2008). CuIn<sub>x</sub>Ga<sub>1-x</sub>Se<sub>2</sub> thin films prepared by electron beam evaporation. Journal of Solar Energy Materials & Solar Cells, 92 pp. 571-575.
- [8] Uhl, A. R., Romanyuk, Y. E. and Tiwari, A. N. (2011). Thin film Cu (In,Ga)Se<sub>2</sub> solar cells processed from solution pastes with polymethyl methacrylate binder. Thin Solid Films 519, 7259–7263.
- [9] Ding, S. J. et al. Tunable Assembly of Vanadium Dioxide Nanoparticles to Create Porous Film for Energy-Saving Applications. Acs Appl. Mater. Inter. 5, 1630–1635.
- [10] Shay, J. L. and Wernick, J. H. (1975). Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications, Pergamon, New York.