

# Growth and Characterization of CuS-Sb<sub>2</sub>S<sub>3</sub> Heterojunction Thin Films.

P.U. Asogwa, Ph.D.

Department of Physics and Astronomy, University of Nigeria, Nsukka, Nigeria.

E-mail: [puasogwa@yahoo.com](mailto:puasogwa@yahoo.com)

## ABSTRACT

A heterojunction of CuS-Sb<sub>2</sub>S<sub>3</sub> thin films have been deposited on glass slide by chemical bath deposition technique (CBD) at room temperature. CuSO<sub>4</sub> and thiourea were taken as the source of the copper ions and sulphide ions, respectively, with TEA as the complexing agent for the deposition of CuS thin film. Sequential deposition of Sb<sub>2</sub>S<sub>3</sub> on glass-CuS substrate was then followed to obtain CuS-Sb<sub>2</sub>S<sub>3</sub> heterojunction. The films were characterized using x-ray diffractometer, energy dispersive fluorescence spectrometer and Unico UV-2102 PC Spectrophotometer. Optical studies reveals that deposition time has significant effect on the absorbance, transmittance and band gap energy of the films. The band gap energy of the films are in the desire interval for their application as window layer for solar cell fabrication.

(Keywords: band gap, CBD, heterojunction, semiconductor devices, optical properties, thin films)

## INTRODUCTION

The study of thin films is an investigation in pure science, since in the film state some new specific effects, which are not applicable to bulk materials, may occur. Quantum Size Effect (QSE) is one of these specific effects, which occurs in films with thickness comparable with effective De-broglie wavelength of the carriers ( $d \sim \lambda$ ).

The technology of thin films deals with the films of thickness between 1 – 100nm. The pivotal role of thin film technology in the development of such a diverse and challenging properties as microelectronics, optical coatings and integrated optics, thin film superconductivity and quantum engineering and solar energy conversion devices is well known and is now recognizes as a frontier area of micro-science and micro-technology. QSE begin to dominate the physical phenomenon as

the size of the material is reduced in one, two and three dimensions. This can be achieved using physical and chemical deposition techniques. A better understanding of particular deposition technique is obtained by employing it to grow a certain material and studying the structural, optical and electrical properties of the material in thin film form [4,5].

The emerging technology needs various types of thin films for variety of applications [1,2,3]. The thin film can be made of multi-component, alloy/compound or multi-layers coatings on the substrates of different shapes and sizes [6,9]. A heterojunction is formed by joining two layers of semiconductors with differing band-gap energies. When the layers have the same conductivity type an isotype heterojunction is formed, whereas in an anisotype heterojunction, the layer conductivity type differs.

Thin films of copper chalcogenides (S/Se)<sub>2</sub> of multinary compositions containing indium (In) or indium and gallium (In<sub>1-x</sub>Ga<sub>x</sub>) are being pursued vigorously as candidate materials for solar cell application due to their band gaps in the appropriate region for high efficiencies of conversion [11]. There is also an ongoing effort to look into the prospects of other absorber materials involving copper, so that the p-type conductivity originating from copper deficiency can be utilized to produce p-type absorbers as an alternative to Cu(In/Ga) (S/Se)<sub>2</sub> [10].

## EXPERIMENTAL DETAILS

Glass microscope slides were cleaned by degreasing them in concentrated hydrochloric acid for 24 hours, washed in detergent solution, rinsed in distilled water and dried in oven at 30°C above room temperature. The bath constituents for deposition of copper sulphide (CuS) thin films were copper sulphate (CuSO<sub>4</sub>) as a source of Cu<sup>2+</sup>, thiourea [(NH<sub>2</sub>)<sub>2</sub>CS] as a source of sulphide

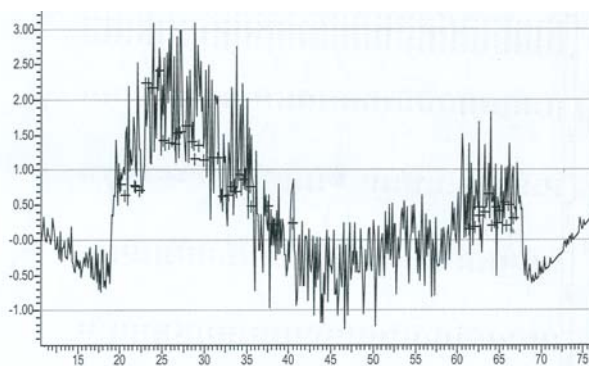
ions ( $S^{2-}$ ) in the presence of triethanolamine (TEA) as the complexing agent. In a typical deposition bath, the solution was composed of 5ml of 1M  $CuSO_4$ , 2.5ml of 60% (TEA), 5ml of 1M thiourea and 3ml of 30%  $NH_3$  put in that order. The solution was then made up to 50ml with distilled water. The deposition was allowed to proceed at room temperature for different dip time of 3.0hrs, 5.0hrs, 7.0hrs, 9.0hrs and 11.0hrs. At the expiration of each dip time, the coated substrate was removed, washed well with distilled water and allowed to dry. The glass-CuS system was used as the substrate for the deposition of  $Sb_2S_3$  film. To achieve this, 5ml of acetone was used to dissolve 1.3g of  $SbCl_3$  in 50ml beaker. This was followed by sequential addition and stirring of 25ml of 1M  $Na_2S_2O_3$  and 34ml of distilled water. The deposition was allowed to proceed at room temperature and was completed in 1.0hr dip time. The coated substrate was removed from the bath and washed with distilled water and dried.

### THIN FILM CHARACTERIZATION

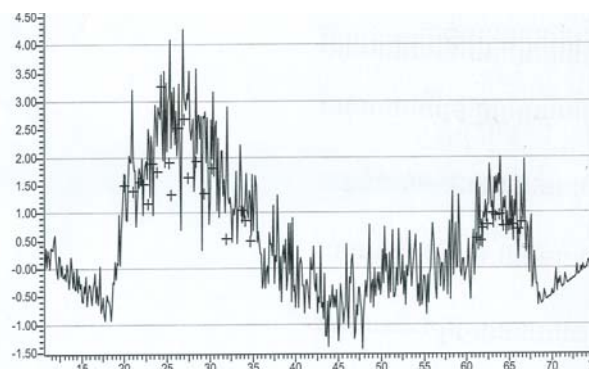
The structure of the film was studied with optical microscope and Philips PW 1500 XRD. The composition of the films was determined by using energy dispersive x-ray fluorescence (ED XRF). The band gap of the films was determined by using the absorbance and transmittance measurement from Unico-UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1000nm.

### RESULT AND DISCUSSION

**X-Ray Diffraction Study:** Typical XRD diffractograms of  $CuS-Sb_2S_3$  heterojunction thin film are presented in Figure 1 a-b. The pattern for the film displayed diffraction peaks at  $2\theta$  values of approximately  $20.00^\circ$ ,  $24.28^\circ$ ,  $25.20^\circ$ ,  $26.96^\circ$ ,  $30.21^\circ$ ,  $33.63^\circ$ ,  $64.84^\circ$ . The presence of identifiable peaks in the diffractograms suggests that the films are not amorphous but crystalline in nature. A close observation of the figures shows an improvement in the crystallinity of the films as dip time increases. It has been reported that as deposition time increases, the thickness of the film increases as well and this leads to improvement in the crystallinity of the film [6].



**Figure 1a:** XRD pattern of  $CuS-Sb_2S_3$  Heterojunction Thin Film at 3 hr. dip time.



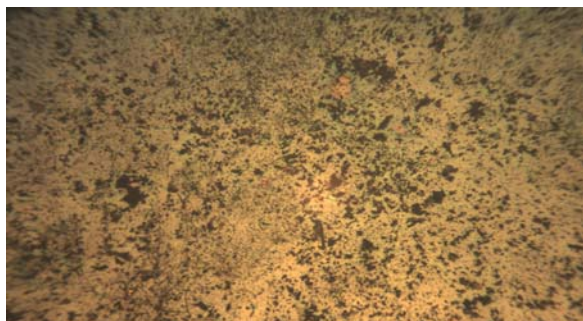
**Figure 1b:** XRD Pattern of  $CuS-Sb_2S_3$  Heterojunction Thin Film at 9 hr. dip time.

A comparison of the spectra of the two films in (a) and (b) show that there is more crystallization and better orientation of the crystal growth in the case of the film deposited at higher dip time.

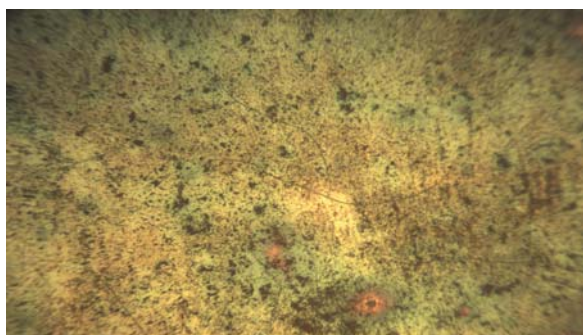
The grain sizes is estimated using the well-known Scherrer relation,  $D = k\lambda / \beta \cos\theta$ , where  $k$  is a constant taken to be 0.94 and  $\lambda$ , the wavelength of X-ray used ( $\lambda = 1.54\text{\AA}$ ). The mean crystallite size calculated from the Scherrer relation lie within the range of 24.8 – 48.9nm

**Photomicrography Study:** The surface microstructure of the films were obtained by taking the photomicrographs of the films coated on the transparent glass slides with wide KPL-W10x/ 18 Zeiss Standard 14 photomicroscope with M<sub>35</sub> 4760+2-9901 camera at a magnification of X200. The photomicrographs of the films are displayed in plates 1-2. A close observation of the optical micrographs of  $CuS-Sb_2S_3$  thin films show a decrease in grain size as dip time increases.

The decrease in grain size as dip time increases may be due to the function of the complexing elements during reaction. This accelerates the chemical deposition reaction in such a way that acceleration causes a decrease in the grain size.



**Plate 1:** CuS-Sb<sub>2</sub>S<sub>3</sub> Thin Film at 3.0 hr. dip time.



**Plate 2:** CuS-Sb<sub>2</sub>S<sub>3</sub> Thin Film at 9.0 hr. dip time.

**Composition Study:** The elemental composition and chemical states of the films under study was analyzed by Energy dispersive x-ray fluorescence (EDXRF). The EDXRF of CuS-Sb<sub>2</sub>S<sub>3</sub> heterojunction thin films deposited at 3.0hrs and 9.0hrs dip time are shown in Table 1.

**Table 1a:** CuS-Sb<sub>2</sub>S<sub>3</sub> Thin Film at 3 hr. dip time.

Analyzed elements:				
El	counts	compd.	conc	
K Ka	2366±71	K	1.455 ± 0.539	%w
Ca Ka	20249±31	Ca	3.748 ± 1.316	%w
Ti Ka	1320±47	Ti	461.409±183.923	ppm
Mn Ka	335±48	Mn	42.47 ± 16.042	ppm
Fe Ka	227±109	Fe	1129.92±396.227	ppm
Ni Ka	579±57	Ni	90.610± 34.250	ppm
Cu Ka	2593±76	Cu	512.653±180.103	ppm
Zn Ka	596±60	Zn	155.330±56.946	ppm
Sr Ka	253±46	Sr	172.249±72.941	ppm
Cd La	1613±18	Cd	8631.66±2615.98	ppm
Sb La	8716±16	Sb	2.259 ± 0.056	%w
Pb La	1199±18	Pb	5.067 ±689	%w

**Table 1b:** CuS-Sb<sub>2</sub>S<sub>3</sub> Thin Film at 9 hr. dip time.

Analyzed elements:				
El	counts	compd.	conc	
K Ka	2187±66	K	1.345 ± 0.497	%w
Ca Ka	20478±299	Ca	3.790 ± 1.32	%w
Ti Ka	969±42	Ti	338.716± 135.733	ppm
Mn Ka	42±47	Mn	43.362 ± 16.777	ppm
Fe Ka	8877±106	Fe	1087.068±380.998	ppm
Ni Ka	708±57	Ni	110.798± 41.605	ppm
Cu Ka	2805±76	Cu	554.567 ±194.550	ppm
Zn Ka	535±57	Zn	139.432± 53.583	ppm
Sr Ka	367±46	Sr	249.864± 92.766	ppm
Cd La	1199±134	Cd	6416.225±1580.82	ppm
Sb La	5068±152	Sb	1.314 ± 0.045	%w
Pb La	6111±39	Pb	7.893.600	%w

The concentration of Cu and Sb can be seen in Table 1a and 1b. The presence of sulphur cannot be detected by the instrument used for this analysis. Other elements present in the table may have come from the glass slide used for the deposition of the films.

## OPTICAL STUDIES

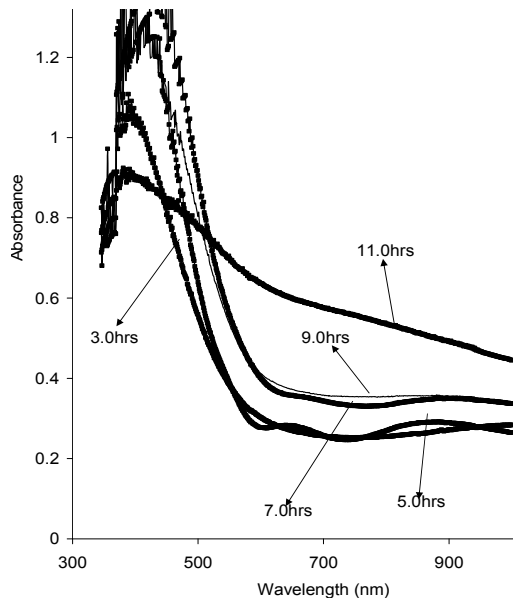
### Variation of the Absorbance and Transmittance of the Films with Wavelength:

Figures 2 & 3 are plots of absorbance vs. wavelength and transmittance vs. wavelength for CuS-Sb<sub>2</sub>S<sub>3</sub> thin film grown in this work. From the absorption spectra of the films displayed in Figure 2, we observe that the absorption edge of the films shift towards shorter wavelength (blue shift) with increasing dip time. Again, absorbance decreases with increasing wavelength, with the highest absorbance occurring in the VIS region of the solar spectrum.

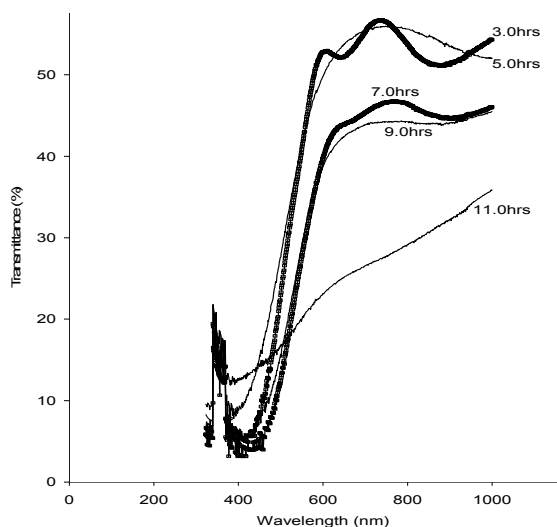
Figure 3 shows that transmittance of the films generally increase with wavelength and decrease with dip time. The observed differences in transmission are only due to difference in thickness. The property of high transmittance in the IR spectrum exhibited by the films is ideal for their use in the construction of poultry roofs and walls.

### Study of Band Gap as a Function of Photon Energy:

Figure 4 shows typical curves of the energy versus the squared absorption coefficient for thin films of CuS-Sb<sub>2</sub>S<sub>3</sub> heterojunction. The fundamental absorption which corresponds to the electron excitation from the valence band to the conduction band can be used to determine the nature and value of the optical band gap.



**Figure 2:** Absorbance vs Wavelength for CuS-Sb<sub>2</sub>S<sub>3</sub> Thin Films.



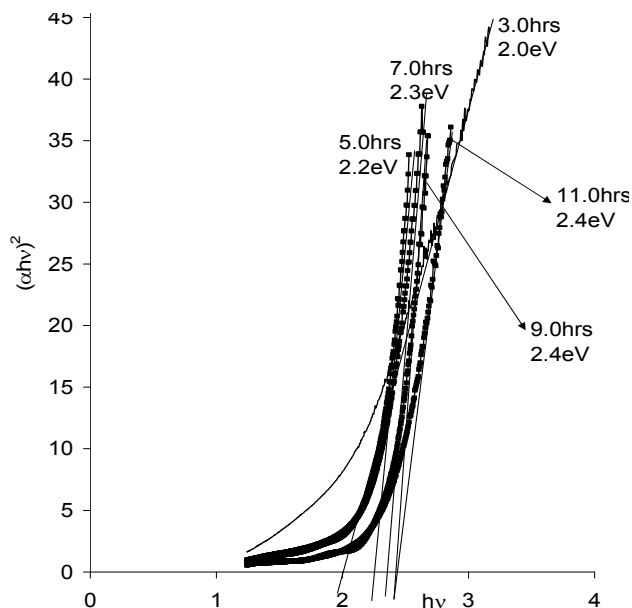
**Figure 3:** Transmittance vs. Wavelength for CuS-Sb<sub>2</sub>S<sub>3</sub> Thin Films.

The relation between the absorption coefficient ( $\alpha$ ) and the incident photon energy ( $h\nu$ ) can be written as:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

where A is a constant,  $E_g$  is the band gap of the material and the exponent n depends on the type of transition. The values of n for direct allowed, indirect allowed and direct forbidden transition are  $n = 1/2, 2, 3/2$  respectively. The direct band gap of

the films were obtained from the linear portion of  $(\alpha h\nu)^2$  versus  $h\nu$  plot as shown in Figure 4.



**Figure 4:** Plot of  $(\alpha h\nu)^2$  vs.  $h\nu$  for CuS-Sb<sub>2</sub>S<sub>3</sub> Thin Films.

We can infer from Figure 4 that as dip time increases, the thickness of the films increase as well and this leads to decrease in band edge sharpness and an increase in energy gap. At critical deposition time, the band gap value remains constant irrespective of the increase in the dip time. However, Sb<sub>2</sub>S<sub>3</sub> thin film deposited on glass slide by chemical bath technique has been reported to behave differently [8,12]. That is, the band gap energy decreases with increasing dip time.

## CONCLUSION

A heterojunction thin film comprising of CuS-Sb<sub>2</sub>S<sub>3</sub> have been successfully deposited onto glass slide using chemical bath deposition technique.

The optical studies showed that most of the films have high absorbance in the VIS region of the solar spectrum and high transmittance in the NIR region and therefore can be used as solar control device or selective absorber surface device. The film could also be applied as anti-dazzling coatings in car windscreen and driving mirrors to

reduce the dazzling effect of light at night. Again, the band gap values exhibited by the films are in the desired interval for their application as window layers for solar cell fabrication.

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## ABOUT THE AUTHOR

**Dr. P.U. Asogwa** is a member for the faculty of the Department of Physics and Astronomy, University of Nigeria, Nsukka (P.O. Box 440001, Nsukka, Nigeria). Dr. Asogwa's research interests include semiconductor materials and thin film characterization.

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