

EFFECTS OF DIP TIME ON THE GROWTH AND PROPERTIES OF CHEMICAL BATH DEPOSITED COPPER ANTIMONY SULPHIDE THIN FILMS

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Chemical bath deposition technique (CBD) has been used to grow CuSbS_2 on plane glass substrates at room temperature. Precursor chemicals: SbCl_3 , $\text{Na}_2\text{S}_2\text{O}_3$ and CuCl_2 were used and reactions took place in chemical reaction baths where the parameter varied was dip time. The effect of this variation on structural, optical and morphological thin film properties were studied. Rutherford backscattering analysis was used to obtain the thin film thicknesses as well as the elemental compositions, X-ray diffraction was used to obtain thin film structures, optical interference microscopy was used to study film surface morphology and spectrophotometric analysis was used to obtain optical properties of films. Such studies revealed CuSbS_2 thin film thicknesses in the range 540 – 575 nm that depended on dip time. Well ordered films grew from dip time of 3 to 6 hrs and such films exhibited direct band gaps of 1.60 to 3.20 eV that also depended on dip time. This heavy dependence of film properties on deposition time implied that growth timing could be used to tailor film properties for various electronic and solar energy device applications.

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1. Introduction

Copper antimony sulphide thin films have been successfully grown at various time using various techniques like spray pyrolysis [1], annealing stack Sb_2S_3 -CuS films freshly grown using chemical bath deposition technique [2] and direct chemical bath deposition synthesis [3]. In recent times, there has been a renewed interest in CuSbS_2 thin films mainly due to its promise for use as good alternative to CuInSe , CuGeSe and CdTe as an absorber layer in solar cell technology [4-5]. Its wide band gap allows an accommodation of much solar energy. Also, copper antimony sulphide and other metal-metal chalcogenides are subjects of great interest in the search for new semiconductor materials for efficient solar energy conversion through photo-electrochemical solar cells [6]. The chemical bath deposition (CBD) techniques, which is used in this work, is cheap, reproducible and particularly available for large area thin surface applications [7-8]. The CBD method relies on the fact that, without application of external fields, thin film can be grown on both metallic and non metallic substrates by dipping them into a suitable reaction baths that contain metallic salts. Though CBD technique has been very successful in growing many ternary thin films [9-12], its success in growing films involving Sb_2S_3 has been achieved hitherto mainly by the annealing of chemically deposited stacks of Sb_2S_3 and another metallic sulphides [13]. In this work, a direct deposition of ternary CuSbS_2 was achieved from solutions bearing Cu, Sb and S ions.

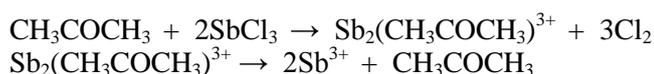
2. Experimental Details

A chemical reaction 50 cm³ beaker bath was set up onto which 1.1 g of Sb_2Cl_3 , dissolved in 8 ml acetone was introduced. Also 6 ml of 1.1 M CuCl_2 , 15 ml of 1.5 M $\text{Na}_2\text{S}_2\text{O}_3$ and 18 ml of

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distilled water were measured onto the beaker while stirring vigorously. Acetone dissolved the water insoluble antimony chloride and also complexed it to ensure slow release of Sb^{3+} . Cu^{2+} came from CuCl_2 and Na_2SO_3 provided S^{2-} . Plane glass slides, pre-cleaned by degreasing them in concentrated hydrochloric acid for 24 hours, washing them in detergent solution, rinsing them in distilled water and drip drying them in free air were used as substrates. Such substrate were inserted onto the solution through a synthetic foam that rested on top of the beaker to support the slide and also protect the solution from dusts.

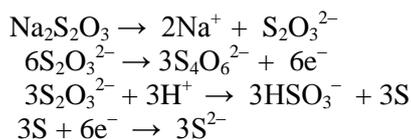
There was precipitation of CuSbS_2 and the precipitation rate was slowed down by the complexing agent to ensure orderly growth. The CuSbS_2 precipitate formed as crystallite grains on the glass and these grains later developed into a continuous film layer after a reasonable dip period. The complexation caused a slow release of Sb ions as follows:



Copper ions were derived from copper chloride as follows:



Also, sulphur ions were derived from sodium thiosulphate as follows [14]:



There was adsorption of $\text{Sb}_2(\text{CH}_3\text{COCH}_3)^{3+}$ complex on the surface of the glass substrate where ionic exchange with Cu^{2+} and S^{2-} resulted in a nucleation that gradually grew into the continuous CuSbS_2 crystal. The reaction which took place at room temperature was maintained for different reaction times (dip times) to study the effect of reaction time on the growth and characteristics of the films. Five similar baths 31A, 31B, 31C, 31D and 31E containing similar chemicals and substrates were therefore set up and allowed at same room temperature of 300K and same initial pH of 8.7 but at different dip times as given in table 1.

Table 1. Variation of dip time for CuSbS_2 films.

| Slide No. | Dip time (hr) |
|-----------|---------------|
| 31A | 1 |
| 31B | 2 |
| 31C | 3 |
| 31D | 4 |
| 31E | 5 |

The surface micrographs of the films were taken at magnification 1000X and a Rutherford backscattering (RBS) analysis based on proton induced X-ray emission (PIXE) technique was used to decipher the elements in both the deposits and glass substrates including the elements percentage abundances. The films structures were studied using a Philips X'Pert PRO diffractometre that used Cu K_α radiator of $\lambda = 0.15406$ nm to scan each sample thin film continuously from $2\theta = 10^\circ$ to 99° in step size of about 0.02° at a room temperature of 288 K. The optical characteristics were studied using a UNICO UV-2102PC spectrophotometer in the wavelength range of 200-1100 nm

3. Results and discussions

3.1 Morphology

Figs. 1a – 1c show the microstructure of CuSbS_2 thin films samples 31A, 31B, and 31D deposited for 1, 2 and 4 h respectively. The samples show less pin holes as deposition time increased suggesting that crystals of greater order developed as deposition time increased. This was also confirmed in XRD results (Fig. 3 – 4) which show clearer peaks for films grown at more dip times.

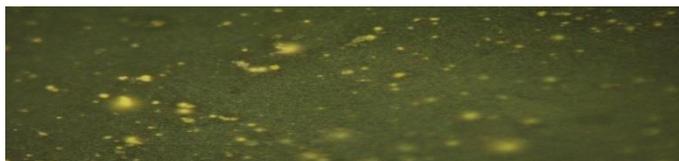


Fig. 1a. Morphology of thin film grown for 1 hr



Fig. 1b. Morphology of thin film grown for 2 hr



Fig. 1c. Morphology of thin film grown for 4 hr

3.2. Compositional Study

The thin films were subjected to Rutherford backscattering analysis which deciphered the elements in the thin film (Layer 1) as well as in the substrate (Layer 2) including the elements percentage abundances as presented in table 2. Higher dip time apparently favoured higher Cu abundance. The RBS also deciphered film thicknesses which were seen to vary with the deposition time as shown in Fig. 2. The thickness increased sharply up to 576 nm in the first 2 min., before decreasing gradually to a stable value of about 560 nm. This initial increase is expected since solution growth requires that ions (Cu^{2+} , Sb^{2+} and S^-) be available and migrate to the glass surface where they combine to form thin films. This increase was however gradually checked by dissolution which set in and indeed balanced off the growth rate after a critical time of 4hr.

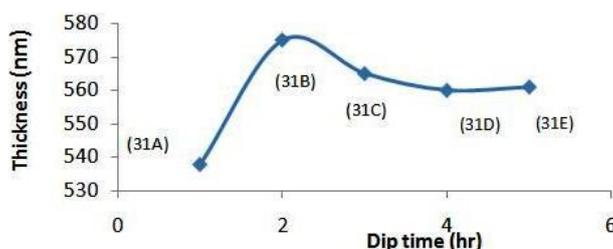


Fig. 2 Thickness vs dip time for copper antimony sulphide

Table 2: Elemental composition of thin films grown at different dip times

| Dip time(hr) | Abundance of elements in the thin film (%) | | |
|--------------|--|-----|------|
| | Cu | Sb | S |
| 1 | 20.2 | 6.0 | 74.3 |
| 2 | 25.4 | 4.2 | 70.5 |
| 3 | 25.8 | 4.0 | 71.3 |
| 4 | 25.9 | 3.9 | 69.7 |
| 5 | 25.9 | 3.9 | 69.8 |

3.3. X-Ray Diffraction Study

The results of X - ray studies done on the films were as shown in figures 3 and 4. They show clear patterns and diffraction lines which are more pronounced for films grown at higher dip time. The diffracton lines were matched to JCPDS card number 01-070-0987 to reveal CuSbS_2 with preferred orientation at 25.66° which was at (1 0 1) plane. These result indicate formation of films of greater crystallinity at higher dip times. Scherrer's formular [15-16]:

$$D = \frac{0.89\lambda}{\beta \cos\theta} \quad (1)$$

was used to estimate the average grain size, D of the crystal where λ is the wavelength of X-rays, β the full width at half maximum (FWHM) of the peak with the highest intensity and θ is the diffraction angle. Such grain size varied from 31.30 nm to 45.52 nm averaging to 35.46 nm.

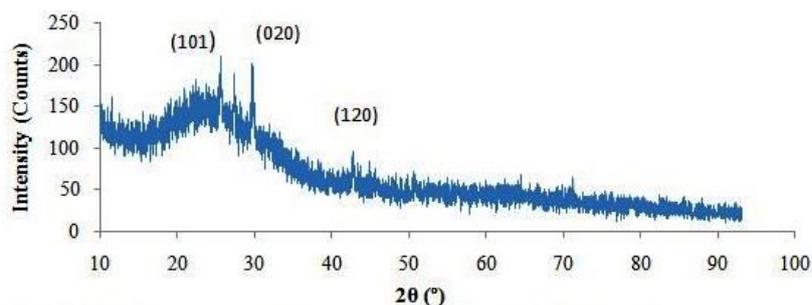


Fig. 3. XRD pattern for copper antimony sulphide thin film of 1 hour dip time

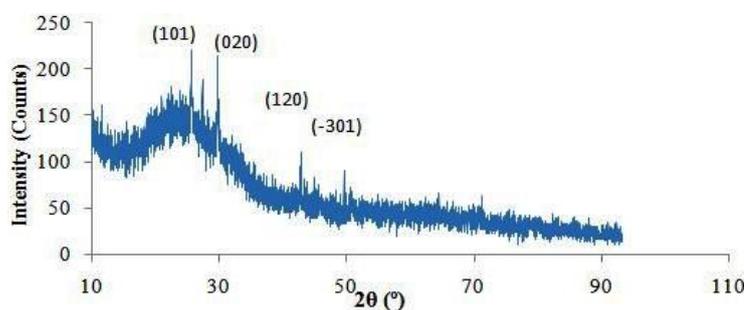


Fig. 4. XRD pattern for copper antimony sulphide of 3 hour dip time

Equation 1 was used to calculate the crystal grain size, D when the wavelength of the incident X-ray was λ , β was the full width at half maximum of X-ray diffraction peaks and θ was the angle at which diffraction occurred. The obtained value of grain size which was 31.94 nm was not in very good agreement with a value of 19.56 nm obtained by other researchers in 2010 [3].

3.4. Optical Studies of Thin Films

The spectral absorbance of the thin film of dip time 3hours is as shown in Fig. 5.

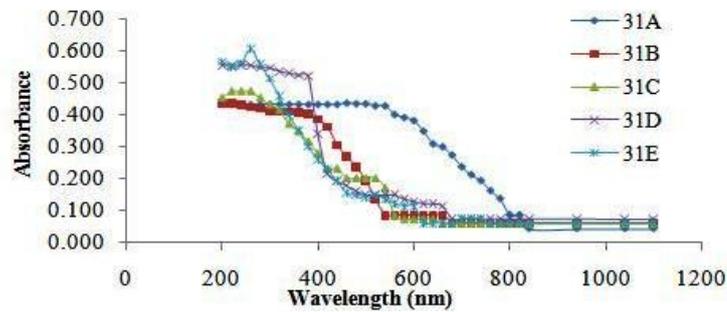


Fig. 5. Spectral absorbance of copper antimony sulphide grown in various dip times

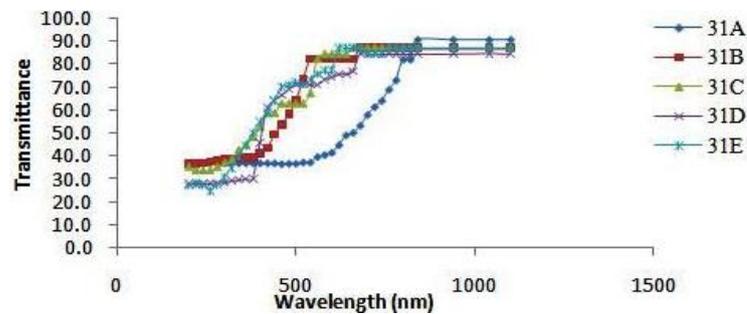


Fig. 6. Spectral transmittance of copper antimony sulphide grown in various dip times

From the absorbance records, the film transmittance, reflectance and energy band gaps were calculated, knowing the film thickness. The transmittance and reflectance plots are as shown in Fig. 6 and 7 respectively. The band gap was deciphered from a graph of $(\alpha h\nu)^2$ against photon energy, $h\nu$ (Fig. 8) by extrapolating the straight line portion of the graph on the $h\nu$ axis. It is well established [17-20] that the absorption coefficient α for direct transition is related to the incident photon energy $h\nu$ as:

$$\alpha = \frac{B(h\nu - E_g)^{n/2}}{h\nu} \quad (2)$$

where E_g is the optical band gap, B is a constant and $n = 1$ if the valence band and the lower part of conduction band are allowed by the selection rules such as in direct band gap transitions of CdS and $n = 3$ if the transitions are forbidden. For allowed transition, we therefore have [21-22]:

$$(\alpha h\nu)^2 = A(h\nu - E_g). \quad (3)$$

where $A = B^2$. The graph of $(\alpha h\nu)^2$ plotted against photon energy, $h\nu$ was linear except for very low photon energy where direct transition is dominated by other forms of transition. However the linear portion of graph was extrapolated to the $h\nu$ axis to obtain the energy band gap, E_g . Such obtained energy band gap varied from 1.60 eV to 3.20 eV and increased as dip time. It can be easily seen that the longer the dip time, the less absorbing the thin films were in the visible ranges. This trend is reflected in the transmittance, A and reflectance, R which are related as:

$$A + T + R = 1 = 1 \quad (4)$$

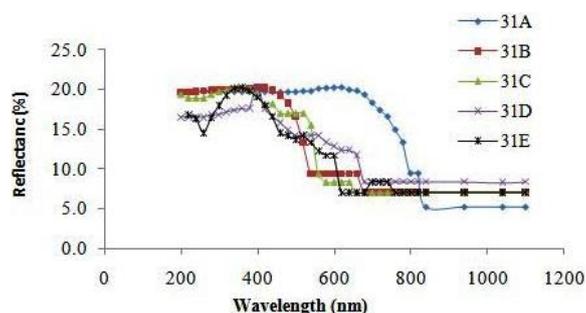


Fig. 7. Spectral reflectance of copper antimony sulphide grown in various dip times

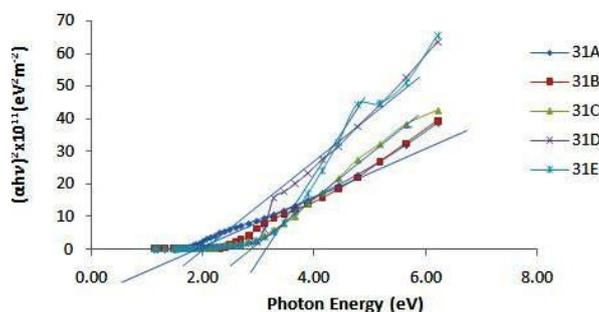


Fig. 8. $(ah\nu)^2$ Vs photon energy for copper antimony sulphide grown in various dip times

4. Conclusion

It has thus been shown that good CuSbS_2 thin films can be grown at room temperature (300 K) at varying dip times using chemical bath deposition technique instead of the usual technique of annealing $\text{CuS-Sb}_2\text{S}_3$ at high temperatures. Films of finer order grew at higher dip times which also favoured higher Cu percentage abundance. The XRD deciphered CuSbS_2 thin film of preferred orientation in the plane (1 0 1) while optical studies revealed band gaps that varied with dip time but all within values between those of CuS and Sb_2S_3 . The absorbance of most of the films grown were high which together with their band gaps make CuSbS_2 suitable as a solar absorber layer in heterojunction photovoltaic cells.

References

- [1] C. S. Liu, L. Chen, X. Niel and R. Yuan. Chalcogenide Letters **11**(12), 639 (2014).
- [2] Y. Rodriguez-Lazcano, M. T. S. Nair and P. K. Nair. Journal of Crystal Growth **223**,399 (2001).
- [3] S. C. Ezugwu, F. I. Ezema and P. U. Asogwa. Chalcogenide Letters **7**(5), 365 (2010).
- [4] M. T. S. Nair, Y. Pena, J. Campos, V. M. Garcia and P. K. Nair. Journal of Electrochem. Soc.**145**, 2113 (1998).
- [5] R. Suarez and P.K. Nair. Journal of Solid State Chemistry **123**, 296 (1996).
- [6] L. Jae-Hyeong, S. Woo-Chang, Y. Jun- Sin and Y. Yeong-Sik. Solar Energy Material **75**, 227 (2003).
- [7] M. N. Nnabuchi. Optical, Solid State and Structural Characterization of Optimized, Grown Thin Films and Their Possible Applications in Solar Energy, Ph.D Thesis, U.N.N. Nigeria (Unpubl.) (2004).
- [8] R. A. Chikwenze. Solution Growth and Characterization of Binary Selenide Thin Films for Device Applications, Ph.D Thesis, U.N.N, Nigeria (Unpubl.) (2012).

- [9] B. Krishnan, A. Arato and E. Cardenas. *Appl. Surf. Sci.* **254**, 3200 (2008).
- [10] R. S. Mane and C. D. Lokhande. *Surf. and Coatings Tech.* **172**, 51 (2003).
- [11] F. I. Ezema, D. D. Hile, S. C. Ezugwu, R. U. Osuji and P. U. Asogwa. *Journal of Non-Oxide Glasses* **2**(2) 121 (2010).
- [12] J.C. Osuwa, I. C. I. Oriaku and F. I. Ezema. *Advances in Natural and Applied Sciences* **3**(2), 247 (2009).
- [13] Y. Rodriguez-Lazcano, L. Guerrero, O. Gomez-Daza, M. T. S. Nair and P. K. Nair. *Superficies y de Vacio*, **9**, 100 (1999).
- [14] J. C. Osuwa and R. U. Osuji, *Chalcogenide Letters*. **8**(9), 571 (2011).
- [15] B. D. Cullity, *Elements of X-ray Diffraction*, Addison Wesley, New York, NY (1978).
- [16] A. B. C. Ekwealor. *Digest J. Nanomater. and Biostructures*, **9**(1), 423 (2014).
- [17] F. Abeles, *Optical Properties of Metals*, North-Holland Pub. Co., Amsterdam (1972).
- [18] J. C. Osuwa, C. I. Oriaku and F. I. Ezema. *Advances in Natural and Applied Sciences*, **3**(2), 247 (2009).
- [19] A. O. Awodugba and A. A. Ibiyemi. *The Pacific Journal of Science and Technology*, **13**(1), 206 (2012).
- [20] A. A. Abu-Shekl, S. Soltan and A. A. Joraid. *Chalcogenide Letters*, **11**(7), 337 (2014).
- [21] F. Haque, K. S. Rahman, M. A. Islam, K. Sopian and N. Amin. *Chalcogenide Letters* **11**(4), 189 (2014).
- [22] C. A. R. Maria Sahayara, A. Mohan, V. Arivazhagan and S. Rajash. *Chalcogenide Letters*, **11**(2), 47 (2014).