ANALYSIS OF ELECTRICAL AND MICRO-STRUCTURAL PROPERTIES OF ANNEALED ANTIMONY SULPHIDE (Sb_2S_3) THIN FILMS.

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Samples of antimony sulphide (Sb_2S_3) thin films synthesized by CBD technique at room temperature and in an oven at 55 ^oC were annealed at temperatures of 100 ^oC, 200 ^oC and 400 ^oC. Surface micro-structural and electrical properties of the thin films were analyzed using Scanning Electron Microscope (SEM), X-Ray Diffractometer (XRD), and a Surface Profiler. Results revealed that some of the films are crystalline while others are amorphous. The film samples deposited at 55 ^oC and annealed at 400 ^oC have crystallite sizes ranging from 0.68 nm – 2.96 nm and inter-atomic spacing that ranged from 1.68411 Å – 6.52829 Å for varying angles of diffraction. Other measurements reported in this paper include high dielectric constants, film thickness and sheet resistance exhibited by the thin films.

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1. Introduction

Chalcogenide thin films have a number of applications in various fields including protective coatings, solar cells, photoconductors, IR detectors, microelectronics etc. [1-6].This has led to increased research in this area culminating in a large body of reports in literature on optical, solid state, structural and electrical properties of chalcogenide thin films of sulphides, tellurides and sellinides [7-10]. Sustained research work is required in order to broaden the specificity of their applications. In this paper we report the effect of annealing on structural and electrical properties of antimony sulphide.

2. Experimental details:

Stoichiometric quantities of antimony trichloride ($SbCl_3$), sodium thiosulphate ($Na_2S_2O_3$) and a complexing agent, acetone (CH_3CO) were prepared in a solution bath followed by the film deposition as follows: 1.3 g of $SbCl_3$ was dissolved in 5ml of acetone in a 50 ml beaker, and then 25 ml of 1M sodium thisulphate was added and stirred before 20ml of H_2O was added to the bath. Degreased glass slides were inserted vertically into the bath with a synthetic foam which partly covered the top of the bath. Deposition in different baths were formed and left for different hours undisturded to check the effect of deposition time. The reaction kinetics for the formation of Sb_2S_3 thin film are as follows:

$$2SbCl_3 + CH_3CO \rightarrow 2Sb[CH_3CO]^{3+} + 3Cl_2$$
$$Sb_2[CH_3CO]^{3+} \rightarrow Sb_2^{3+} + CH_3CO$$
$$Na_2S_2O_3 \rightarrow 2Na^+ + S_2O_3^{2-}$$
$$6S_2O_3^{2-} \rightarrow 3S_4O_6^{2-} + 6e^-$$

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$3S_2O_3^{2-} + 3H^+ \rightarrow 3HSO_3^- + 3S$
$3S + 6e^- \rightarrow 3S^{2-}$
$Sb_2^{3+} + 3S^{2-} \rightarrow Sb_2S_3$

Measurements following the film deposition were performed at Sheda Science and Technology Complex (SHESTCO), Gwagwalada, Abuja with the assistant of technicians. The XRD patterns were obtained using X-pert Panalytical X – Ray Diffractometer using Cu K-Alpha (λ = 1.54060Å) operated at 30mA and 40KV. The microstructural analysis was performed with a Scanning Electron Microscope (SEM), while the film thickness was measured with a surface profiler.

3. Results and discussion

X-Ray Diffractometer (XRD) was used to ascertain a wide variety of structural information of the thin films. The maximum crystallite sizes of the films were estimated using Sherrer's formula

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the wavelength used (1.54060Å), β is the angular width at half maximum intensity in radians and Θ is the Bragg's angle. Values of the XRD measurements are contained in table 1. Figures (1-2) show XRD peaks for Sb_2S_3 thin films deposited at room temperature for unannealed and 100 ^oC annealed samples. The SEM micrographs of the surface images of the Sb_2S_3 thin films deposited at room temperature for as grown sample and sample annealed at 200 ^oC are shown in figures (3,5) while figures (4,6) are surface images for samples deposited at 55 ^oC and annealed at 200 ^oC and 400 ^oC respectively. It is evident that amorphous and crystalline forms of the thin film are produced by the effect of annealing . The sample annealed at 200 ^oC has large crystallite size of 7.49 nm measured at a diffraction angle of 15.8462 degrees.

Table 1 : Some XRD crystallographic properties of Sb_2S_3 thin films deposited at 55 ^oC

Sample	Annealing Temp (^oC)	Angle Θ (degrees)	FWHM (β)	Inter-atomic Distance d(Å)	Constant K	Crystallite Size D(nm)
CB3	200	15.8462	0.09120	2.82104	0.9	7.49
CB5	400	6.7820	0.04725	6.52829	0.9	2.96
"	"	13.7623	0.06300	3.24068	0.9	2.27
"	"	15.968	0.06300	2,80226	0.9	2.23
"	"	22.9352	0.12595	1.97834	0.9	1.20
"	"	27.2190	0.23040	1.68411	0.9	0.68

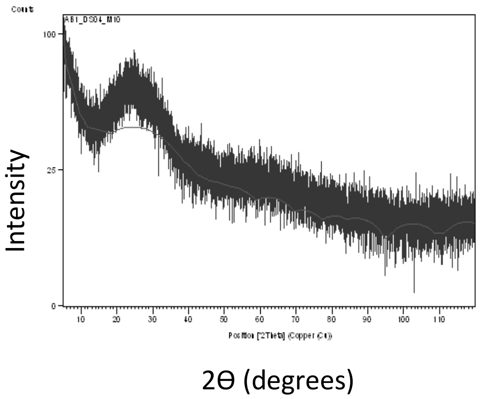

Fig. 1. XRD pattern for Sb_2S_3 thin film deposited at room temperature and unannealed

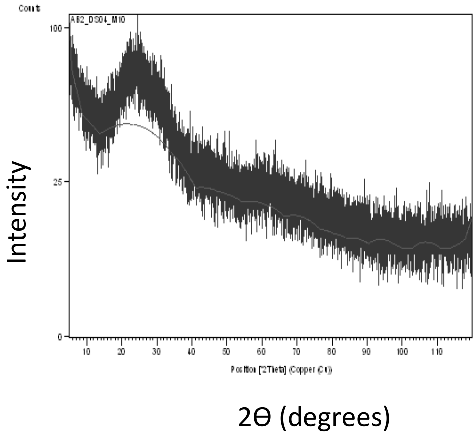

Fig. 2. XRD pattern for Sb_2S_3 thin film at room temperature and annealed at 100 ^oC

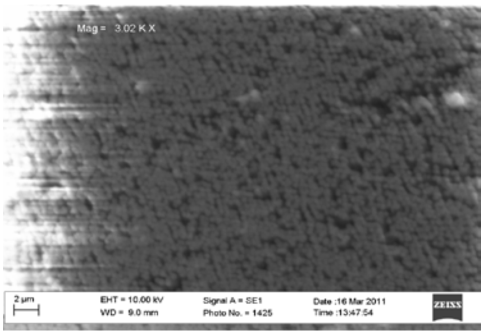

Fig. 3: SEM micrograph of Sb_2S_3 thin film deposited at room temperature and unannealed

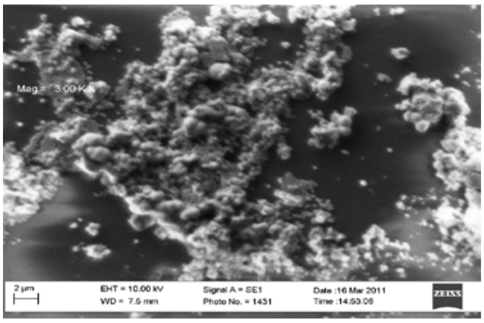

Fig. 4: SEM micrograph of Sb_2S_3 thin film deposited at 55 ^oC and annealed at 200

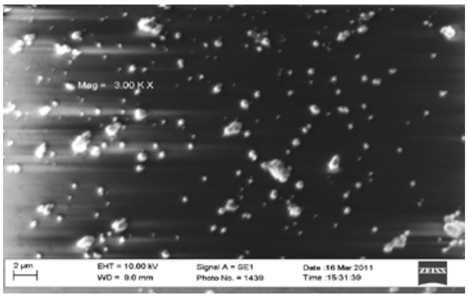

Fig. 5. SEM micrograph of Sb_2S_3 thin film deposited at room temperature, annealed at 200 ^oC

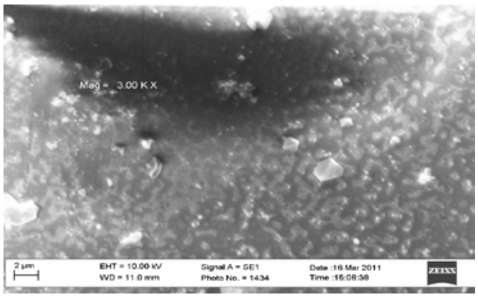

Fig. 6. SEM micrograph of Sb_2S_3 thin film deposited at 55 ^oC and annealed at 400 ^oC

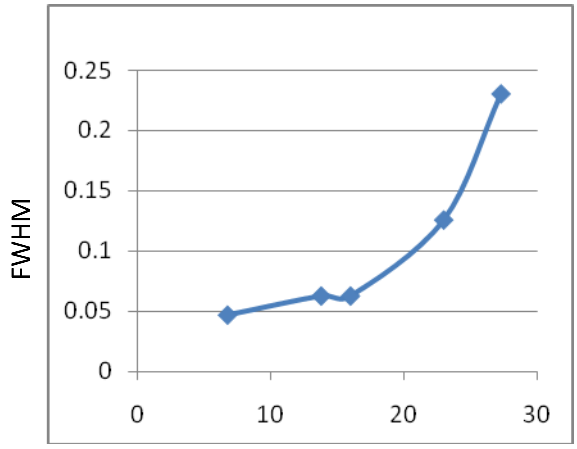

Fig. 7. FWHM as a function of diffraction angle for Sb_2S_3 thin film deposited at 55 ^oC and annealed at 400 ^oC

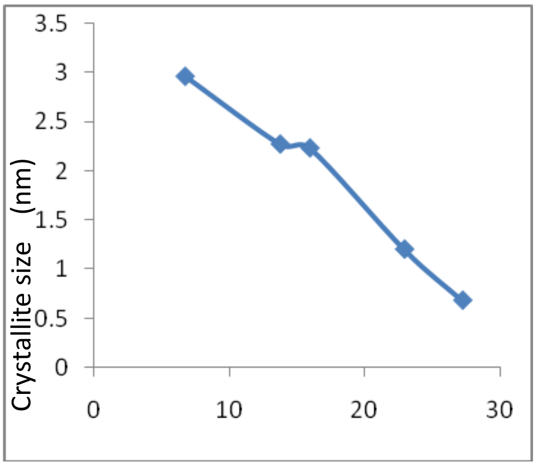

Fig. 8. Crystallite size as a function of diffraction angle for Sb_2S_3 thin film deposited at 55 ^oC and annealed at 400 ^oC

Figures (8, 9) show plots of crystallite size and inter-atomic spacing respectively for varying diffraction angle for the film sample deposited at 55 ^oC and annealed at 400 ^oC. The crystallite size and inter-atomic spacing decrease with increase in diffraction angle while figure 7 shows that the FWHM increases with increase in diffraction angle.

The film thickness was calculated from the lower part of the X-Y charts of the surface profiler shown in figures (10-13). The film resistance, R and sheet resistance, R_s were also calculated using value of V/I given by the surface profiler as follows:

Angle (degrees) $\qquad$ $R = kV/I$ $\qquad$ (2)

where k is a constant (4.523)

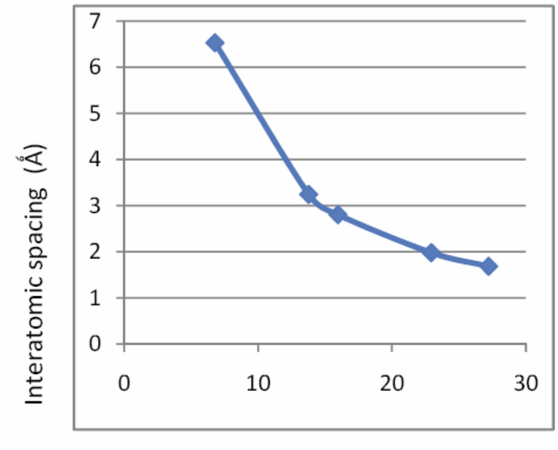

Fig. 9. Inter-atomic spacing as a function of diffraction angle for Sb_2S_3 thin film deposited at 55 ^oC and annealed at 400 ^oC

$$R_s = Rxt \qquad (3)$$

Where t is film thichneess

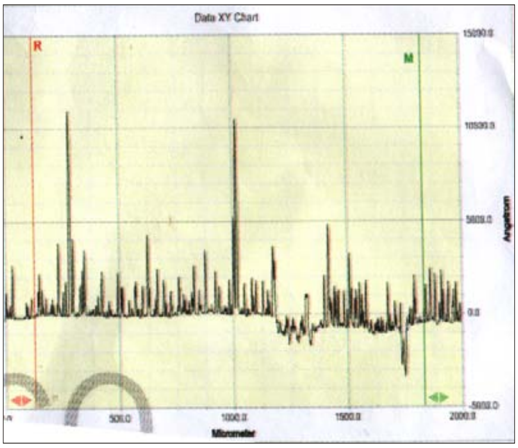

Fig. 10. Surface profile for Sb_2S_3 thin film deposited at room temperature and unannealed (sample AB1)

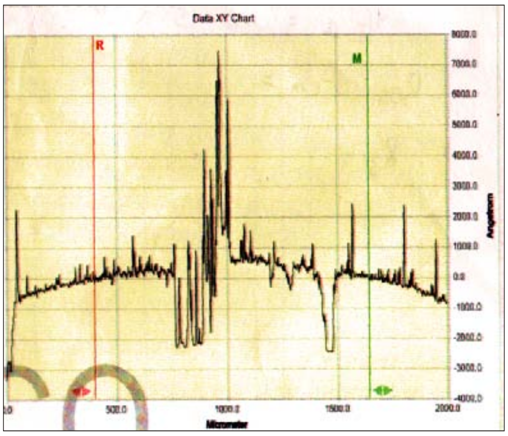

Fig. 11. Surface profile for Sb_2S_3 thin film deposited at room temperature and annealed at 100 ^oC (sample AB2)

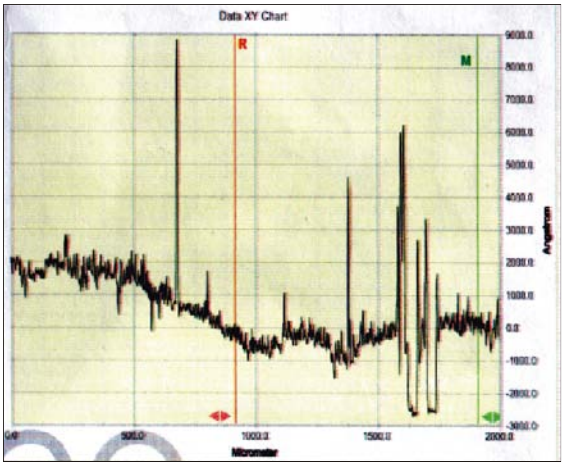

Fig. 12. Surface profile for Sb_2S_3 thin film deposited at 55 ^oC and annealed at 200 ^oC (sample CB3)

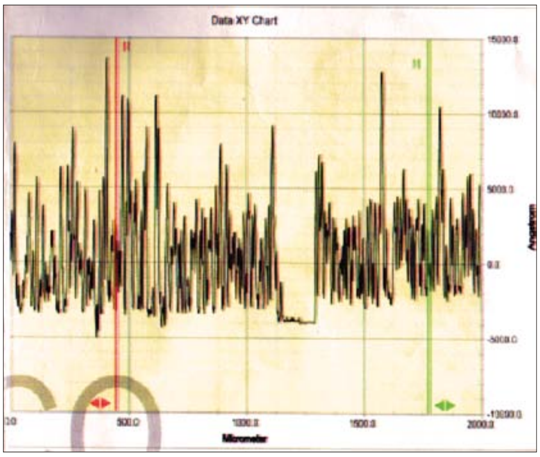

Fig. 13. Surface profile for Sb_2S_3 thin film deposited at 55 ^oC and annealed at 400 ^oC (sample CB5)

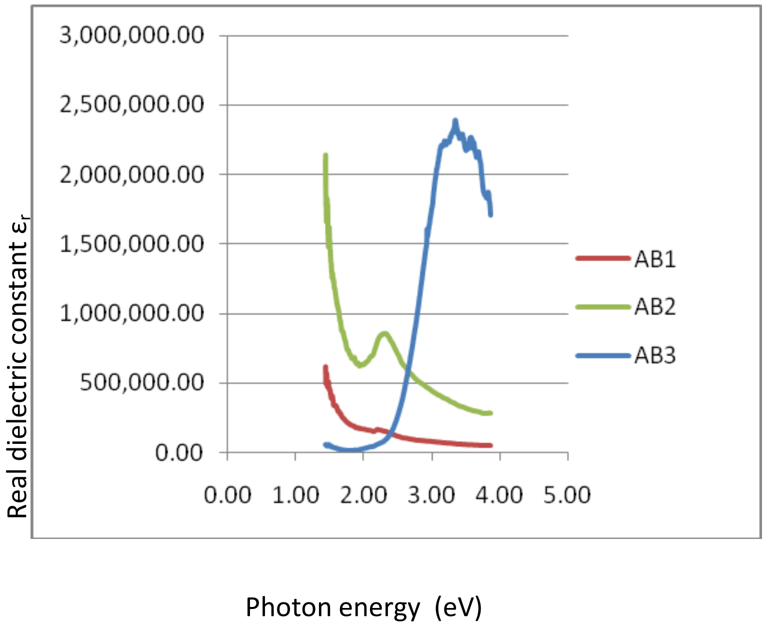

Fig. 14. Real dielectric constant as a function of photon energy for room temp deposition and annealed Sb_2S_3 thin film samples AB1 (unannealed) AB2 (100 ^oC) and AB3 (200 ^OC)

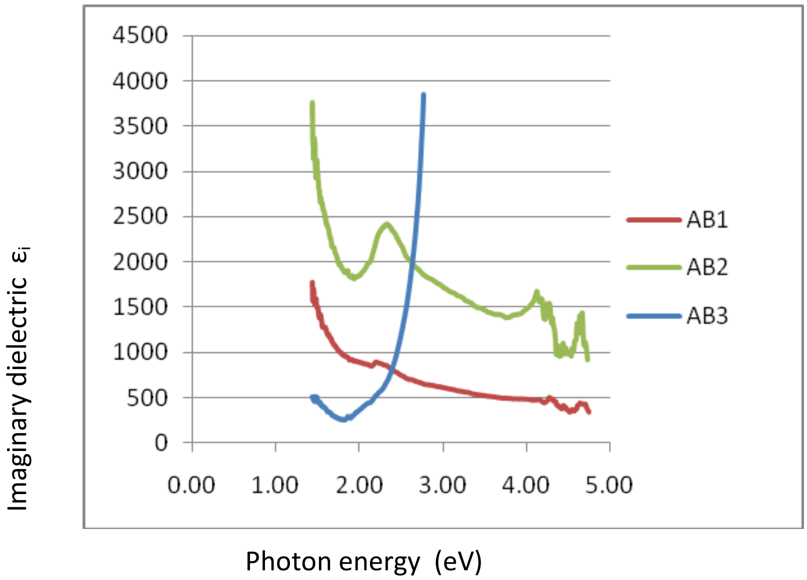

Fig. 15. Imaginary dielectric constant as a function of photon energy for room temp deposition and annealed Sb_2S_3 thin film samples AB1 (unannealed) AB2 (100 ^oC) and AB3 (200 ^OC)

Figures (14,15) show that the real and imaginary dielectric constants, ε_r and ε_i of the Sb_2S_3 thin films increase with annealing. Measurements of other electrical properties and thickness obtained for the thin films are contained in table 2.

Table 2: Electrical properties and thickness of Sb_2S_3 thin film samples

Sample	Deposition Temp (^oC)	Annealing Temp (^oC)	Resistance R x 10^3(Ω)	Sheet Resistance R_s ($\Omega\mu m$)	Thickness t (μm)	ε_r	ε_i
AB1	Room Temp	-	1225733	416.75	0.34	$6.0x10^5$	1580
AB2	Room Temp	100	1243825	298.52	0.24	$2.2x10^6$	3800
AB3	Room Temp	200	1225733	220.63	0.18	$2.4x10^6$	3800
CB3	55 ^oC	200	1239302	334.61	0.27	$2.2x10^6$	3000
CB5	55 ^oC	400	1230256	492.10	0.40	$3.8x10^6$	3000

4. Conclusions

The synthesis and characterization of electrical and structural properties of antimony sulphide thin films have been successfully carried out and qualitative and quantitative results presented. The effects of deposition and annealing temperatures on the properties of Sb_2S_3 thin films were investigated. The variations of inter-atomic spacing and crystallite size with diffraction angle for the thin films have also been presented. The results provide basis for specific applications in such areas as protective coatings, solar cells, photoconductors, IR detectors, microelectronics etc,

References

[1] B. A. Ezeokoye, Journal of Science and Technology **23**(2), 41 (2003)
[2] F,I. Ezema, S. C. Ezeugwu, P. U. Asogwa and A. B. C. Ekwealor, Journal of Ovonic Research **5**(5), 145 (2009)
[3] F. I. Ezema, and M. N. Nnabuchi, Journal of Research (Science) 17(12), 115 (2006)
[4] F. I Ezema, (2004) Journal of the University of chemical technology and metallurgy. **39**(4), 495 (2004)
[5] I. C. Ndukwe, Nigeria Journal of physics Vol. 7 P. **33** (1995).
[6] C.I. Oriaku, F. I. Ezema and J. C. Osuwa, The Pacific Journal of Science and Technology **10**(1), 413 (2009)
[7] J. C. Osuwa, and C. I Oriaku, Journal of Non-oxide Glasses **2**(1), 1 (2010)
[8] J, C. Osuwa, C. I. Oriaku, E. C. Mgbaja, Chalcogenide Letters **7**(12), 679 (2010)
[9] I. E. Ottih, A. J. Ekpunobi, Journal of Basic physical research. Vol. **1**. P. 17 (2010)
[10] A. U. Ubale, V. P. Deshpande, Y. P. Shinde, D. P. Gulwade, Chalcogenide Letters **7**(1), 101 (2010).