Chalcogenide Letters Vol. 13, No. 10, October 2016, p. 451 - 457

COMPOSITIONAL AND OPTICAL ANALYSIS OF CHEMICALLY DEPOSITED ZINC-DOPED ANTIMONY SULPHIDE THIN FILMS

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Thin films of antimony sulphide (Sb_2S_3) were grown using the chemical bath deposition method. The films were then doped using zinc impurities at different concentrations in the range 0.25M to 1.00M. The films were annealed at an annealing temperature of 200 ^oC. The compositional characterization was done using the Rutherford Backscattering techniques. The results show that the film thicknesses increased consistently with an increase in the concentration up to a concentration of 1.00M. However, an increased proportion of trace element possibly from the soda-lime glass substrates were also observed. The optical characterization was done using Fourier transform infrared spectroscopy, and the results indicate that the transmittances of the film were quite high. The film thickness was up to 1.5 μm, which indicate that the films are suitable for use in fabrication of photonic devices especially in photovoltaic solar cell devices.

(Received July 27, 2016; Accepted October 4, 2016)

Keywords: Composition, Rutherford Backscattering, Annealing, Doping

1. Introduction

The potentials of antimony sulphide thin films are currently been investigated by different research groups for applications in different device designs, in nanotechnology, and even in production industries. Antimony sulphide is known to be environmentally safe, and the constituent's elements (antimony Sb, and sulphur S) are abundant and cheap. Another significant advantage of using antimony sulphide in thin film devices lies in its ease of deposition using low cost and efficient deposition techniques. The use of antimony sulphide thin films to fabricate different technological devices has been reported in the literature. For example, thin films of antimony sulphide has been utilized as solar cells [1,2,3,4] switching devices [5], microwave devices [6], opto-electrochemical devices [7], photoconductors [8] and in decorative coatings [9]. Antimony sulphide thin films can be prepared using different low cost deposition techniques. According to the literature, these include the successive ionic layer deposition techniques (SILAR) [4], simple solvothermal and hydrothermal methods [10], atomic layer deposition [11], dip-dry technique [12], thermal evaporation [12], chemical bath deposition technique (Nezu et al, 2010; Gaza et al, 2011), and physical vapour deposition [7]. Chemical bath deposition method is widely used mostly because; (i) it is less expensive compared to the other deposition techniques (ii) it is much easier for large area deposition (iii) the deposition equipment are more common and can easily be sourced locally, (iv) it offers flexibility in fabrication of devices, (v) and most importantly, it also yield high quality films.

In the present report, thin films of antimony sulphide were deposited using the solution growth technique. The specific aim of the study is to investigate the influence of different concentrations of zinc impurities on the compositional properties, in particular the stoichiometry of the doped-antimony sulphide thin films at the different growth conditions, and to finally deduce the possible device applications of the layers.

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2. Materials and methods

In this work, the source of antimony in this experiment was antimony trichloride ($SbCl_3$). Further, to get the $SbCl_3$ solution, 11.5g of $SbCl_3$ was dissolved in 50 ml of acetone. This was also placed in 33 ml of double distilled water. The resulting solution was stirred using a magnetic stirrer for 10 minutes in order to ensure even dissolution of the solutes. The pH of the resulting solution was maintained at 3.5. The glass substrates used in the experiment measuring (16 x 30) mm was ultrasonically cleaned after washing with H_2SO_4 and rinsed with distilled water. The substrate were then introduced vertically into the solution in a 100ml beaker using synthetic foam as the holder. Deposition was allowed to take place for a period of 5 hours at 298K after which the slides were removed and washed with running distilled water and then dried in air. The deposited films were then annealed at 373K at annealing times $\leq$ 6 h, in order to improve the crystallinity of the layers. The composition of the films was investigated using the Rutherford Back Scattering technique, and the transmittance and reflectance versus wavelength measurements was done using Fourier transform infrared spectroscopy.

3. Results and discussion

Fig. 1 gives the variation of the antimony and annealing time with the zinc impurities at the different concentrations. The plot indicates that the annealing time has a linear dependence with the variation of concentration of Sb. However, as the concentration of the zinc impurity increases, the % variation of the Sb increases up to a maximum and then started to decrease. This could be attributed to the gradual displacement of the Sb atoms by the zinc impurity [12]

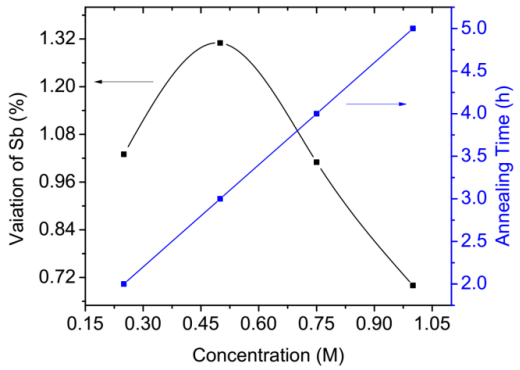

Fig. 1. Variation of Sb (%) and annealing time (h) with zinc impurities (M).

Fig. 2 gives the plots for the composition of the as-deposited films that was doped with zinc impurities (0.25 M) and annealed at annealing time of 2h. The composition indicate that the stoichiometry of the Sb and S were relatively at the required ratio. However the presence of other elements such as oxygen was due to oxidation during the deposition process.

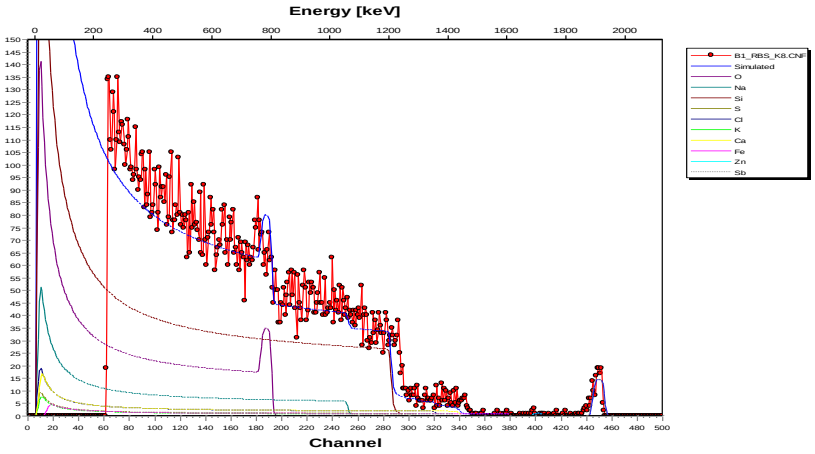

Fig 2 gives the RBS plots of the as-deposited films

Table 1. Composition of the layer shown as Fig. 2

Layer1: Thickness	611.63E15 Atoms/cm^2									
Composition	Sb		O		Zn					
	1.03%		98.73%		0.24%					
Layer 2 (Glass substrate): Thickness	99889.24E15 Atoms/cm^2									
Composition	O	Si	Ca	K	Na	S	Fe	Cl		
	57.80%	28.00%	1.00%	0.05%	10.23%	0.80%	0.27%	1.40%		

The presence of the oxygen could lead to a variation in the intrinsic and extrinsic properties [13]. The addition of the zinc impurities yielded a smooth profile, a possible indication of uniform mixing and deposition. The presence of silicon, calcium, sodium and chlorine were attributed to the chemical reaction between the substrate material and the source constituents.

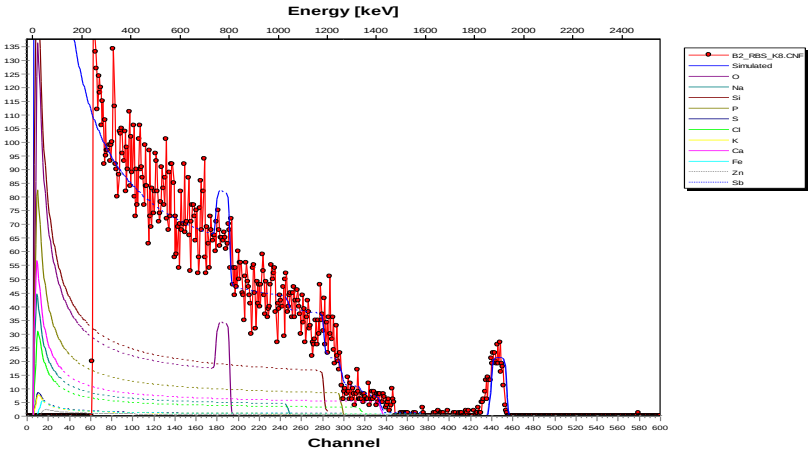

Fig. 3: RBS of the films annealed for 1hour.

Table 2. Composition of the layer shown as Fig. 3

Layer1: Thickness	11611.60E15 Atoms/cm^2									
Composition	Sb 1.31%		O 98.58%		Zn 0.11%					
Layer 2 (Glass substrate): Thickness	99889.24E15 Atoms/cm^2									
Composition	O 57.80%	Si 28.00%	Ca 1.00%	K 0.05%	Na 10.23%	S 0.80%	Fe 0.27%	Cl 1.40%		

Fig. 3 shows the composition plots for the film annealed for one hour, while table 2 is the corresponding composition of the films. The plot as well as the table indicates that annealing for one hour reduces the composition of the Sb by about 28%, while that of zinc and oxygen decreased by about 23% and 15% respectively. This could be attributed to the removal of oxygen by combustion, as annealing helps to remove the hydroxyl group. Figures 4 and 5 and tables 3and 4 show the composition of the films when annealed for 3 and 5 hours respectively.

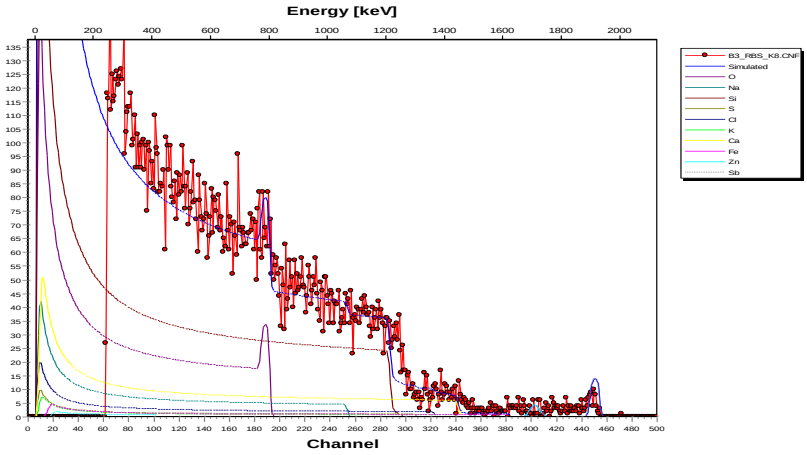

Fig. 4: RBS of the films annealed for 3 hours

Table 3. Composition of the layer shown as Fig. 4

Layer1: Thickness	500E15 Atoms/cm^2									
Composition	Sb 1.01%		O 97.91%		Zn 1.08%					
Layer 2 (Glass substrate): Thickness	99889.24E15 Atoms/cm^2									
Composition	O 57.80%	Si 28.00%	Ca 1.00%	K 0.05%	Na 10.23%	S 0.80%	Fe 0.27%	Cl 1.40%		

The figures and the corresponding tables indicate that annealing the film at different time intervals has profound effect on the composition of the films. Generally, annealing removes the water of crystallization and has effect on the distribution of the particles as well as the dislocation density [14]. These will in turn affect the arrangement of the atoms in the crystals. Similarly as the oxygen atoms are displaced during annealing, the zinc atom tends to fill the void.

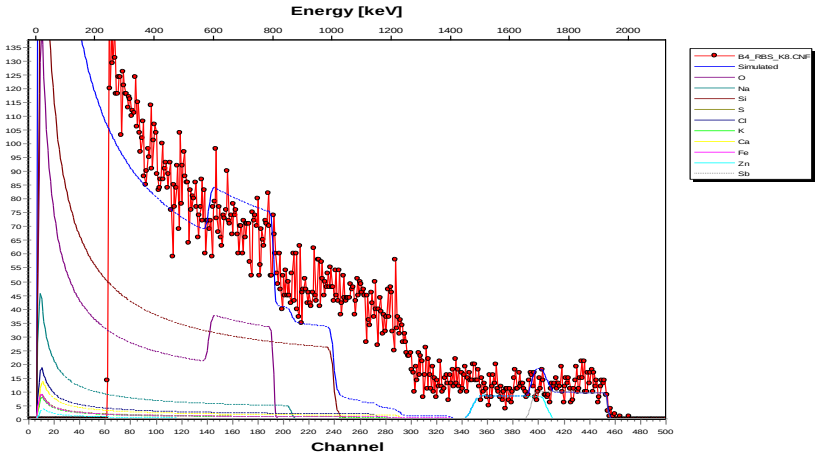

Fig. 5: RBS of the films annealed for 5 hours

Table 4. Composition of the layer shown as Fig. 5

Layer1: Thickness	37777.05E15 Atoms/cm^2									
Composition	Sb		O		Zn					
	0.70%		97.57%		1.73%					
Layer 2 (Glass substrate): Thickness	99889.24E15 Atoms/cm^2									
Composition	O	Si	Ca	K	Na	S	Fe	Cl		
	57.80%	28.00%	1.00%	0.05%	10.23%	0.80%	0.27%	1.40%		

4. FTIR study

For the FTIR measurements, a Schimadzu FTIR spectrometer working in the mid-infrared range from 100 to 4000 cm^{-1} was used. The spectrum was acquired in transmittance mode with a resolution of 1 cm^{-1}. Fig. 6 shows FTIR spectra of as- deposited film. From the spectra, it can be observed that in the region below 100cm^{-1} the film displayed no transmittance, while in the region between 200 to 3600cm^{-1} three peaks at 3507.17 cm^{-1}, 2872.78 and 2357.72 cm^{-1} corresponding to the Sb- Zn-O is noticed. The three peaks are sharp and are also prominent. The existence of isocthiocyanate groups (-N =C= S, Zn-O, Zn-OH and absorbed H_2O in chemical deposited films have been reported by many researchers [13,15,16].

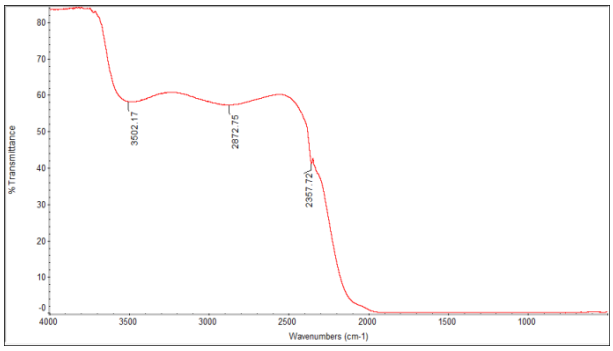

Fig. 6: FTIR of as-deposited films

The FTIR of the film annealed for 1 hour, 3 hours and 5 hours are shown in figures 7, 8 and 9 respectively. In figure 7, the prominent peaks are observed at absorption peaks of 3502.04 cm^{-1}, 2872.78 cm^{-1} and 2357.75 cm^{-1}. These absorption peaks showed little variation from the absorption peaks of the as- deposited films. This is an indication that annealing at 1 hour does not contribute much significant influence on the transmission spectra. However, in figure 8, the absorption peaks of 3502.03 cm^{-1}, 3872.73 cm^{-1} and 2357.51 cm^{-1} were noticed showing a shift of the absorption edge towards the lower wavelength. This could be attributed to the removal of water molecules after annealing of the films at 3 hours. This behavior is collaborated by the composition of the film as displayed in table 2. In fig.9, the absorption peaks are identified at 352.03 cm^{-1}, 2872.88 cm^{-1} and 2357.77 cm^{-1}. The weak peaks observed in all the spectrum could be attributed to the C = S bending modes or the peaks corresponding to the impurities such as Sb – O, Zn – O, Zn- OH or due to the presence of trace amount of adsorbed water that were not removed during annealing etc [13] . This is evident in the as-deposited films having broader peaks. The transmittance of the films were all high irrespective of the annealing time

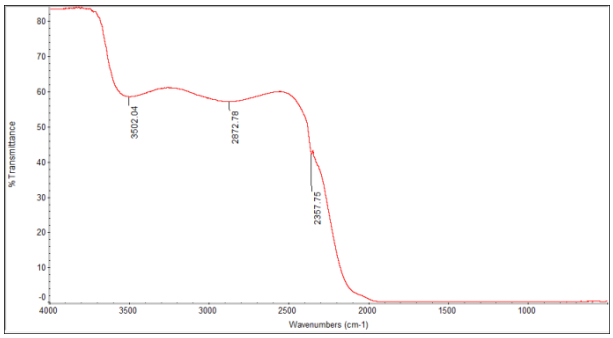

Fig. 8. FTIR of films annealed at 1 hour

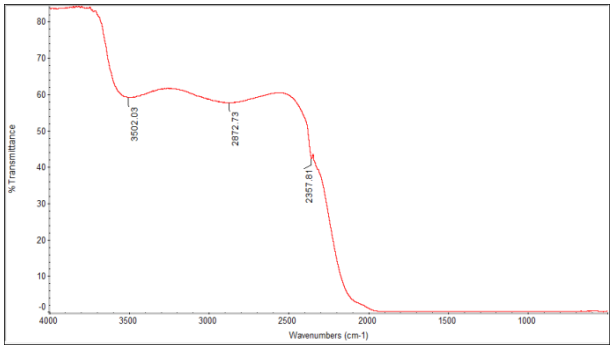

Fig. 8: FTIR of films annealed at 3 hours

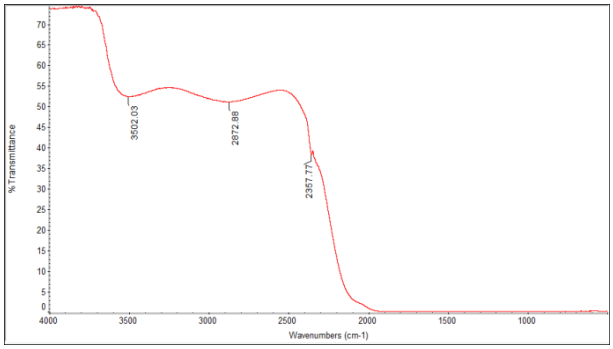

Fig. 9: FTIR of films annealed at 5 hours

5. Conclusion

We used the chemical bath method to deposit thin films of antimony sulphide (Sb_2S_3). The films were then doped using zinc impurities at different concentrations in the range 0.25M to 1.00M. The films were annealed at an annealing temperature of 200 ^oC. The compositional characterization was done using the Rutherford Backscattering techniques. The results show that the film thicknesses increased consistently with an increase in the concentration up to a concentration of 1.00M. However, an increased proportion of trace element possibly from the soda-lime glass substrates were also observed. The optical characterization was done using Fourier transform infrared spectroscopy, and the results indicate that the transmittances of the film were quite high and is dependent on the annealing temperature.

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