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Chemical Bath Deposition of SnS Thin Films: AFM, EDAX and UV-Visible Characterization

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ABSTRACT

In this study, chemical bath deposition has been used to prepare tin sulfide thin films on microscope glass slides from acidic aqueous solution. The effect of bath temperature on the properties of thin films was investigated using atomic force microscopy, energy dispersive X-ray analysis and UV-Visible spectrophotometer. Atomic force microscopy image for the films deposited at 80 °C revealed that all grains uniformly distributed over the surface of substrate indicated well defined growth of SnS material. Optical absorption showed the presence of direct transition and band gap energy decreased from 1.5 to 1.2 eV with the increased of bath temperature from 40 to 80 °C.

Key words: Tin sulphide, Atomic force microscopy, Thin films, Surface roughness, Thickness.

INTRODUCTION

For the last couple of decades, thin films have attracted much interest due to their varied applications such as semiconducting devices, sensor devices, thermo-electric devices, radiation detectors, optoelectronic devices and photovoltaic cells. A variety of techniques such as chemical bath deposition[1], plasma-enhanced chemical vapour deposition[2], reactive sputter deposition[3], molecular beam epitaxy[4], vacuum evaporation[5], pulsed laser deposition[6], successive ionic layer adsorption and reaction method[7], electrodeposition[8], thermal evaporation[9] and electron beam evaporation[10] have been used for deposition of thin films. Among various other methods, the technique of chemical bath deposited thin films has the advantage of being a low cost, simple and efficient growth of the films from aqueous solution. This method has been actively investigated for growth of binary compound such as CdSe[11], Sb_2S_3[12], PbS[13], In_2S_3[14] and MnS[15] while ternary thin films such as $Pb_{1-x}Fe_xS$[16], $CdS_{1-x}Se_x$[17], Cu_4SnS_4[18], $Zn_xCd_{1-x}S$[19] and $ZnIn_2Se_4$[20] by many researchers.

In this paper, synthesis of tin sulphide thin films using chemical bath deposition technique is presented. The tin chloride and sodium thiosulphate were used as the tin and sulphide ions sources, respectively. The influence of bath temperature on the SnS thin films was investigated by atomic force microscopy, energy dispersive X-ray analysis and UV-visible spectrophotometer.

MATERIAL AND METHODS

Microscope glass slides were used as the substrate during the deposition process. The substrates were first cleaned in ethanol solution and subsequently ultrasonically washed with distilled water. Substrates were then dried in an oven at 90 °C. Tin chloride, sodium thiosulphate, disodium ethylenediaminetetraacetate and hydrochloric acid of analytical reagent grade were used as received. Aqueous solutions of tin chloride, sodium thiosulfate and disodium ethylenediaminetetraacetate were separately prepared before experiment. 25 mL of tin chloride (0.2 M) and 25 mL of disodium ethylenediaminetetraacetate (0.2 M) were mixed in a beaker. Then, 25 mL of sodium thiosulphate (0.2 M) was added into mixture and the pH was adjusted to 1.5 by addition of hydrochloric acid. Substrates were immersed vertically in the beaker. In order to investigate the influence of bath temperature on the thin films, the beaker was placed in water bath at desired bath temperatures such as 40, 60 and 80 °C. The beaker was not stirred during the thin films deposition. After completion of films deposition (30 min), the deposited films were then washed with distilled water and dried in air at room temperature.

The surface morphology, surface roughness and thickness were examined by recording atomic force microscopy (AFM) images with a Q-Scope 250 in contact mode with a commercial Si_3N_4 cantilever. The elemental composition of the films was studied by scanning electron microscope (JEOL, JSM-6400) attached with energy dispersive analysis of X-ray (EDAX) analyzer. Optical absorption study was carried out using the Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The film-coated microscope glass slide was placed across the sample radiation pathway while the uncoated microscope glass slide was put across the reference path. The data obtained from the films was used to investigate the band gap energy and transition type of the thin films.

RESULTS AND DISCUSSION

Figure 1 represents the atomic force microscopy (AFM) images of SnS thin films deposited at 40, 60 and 80 °C on microscope glass slides and the scan size is 20 × 20 µm. Study of the atomic force microscopy (AFM) images indicates that at the beginning of growth (40 °C), the grain sizes are very small (0.5 µm). The films show incomplete coverage of material over the surface

Table 1: Film thickness values of SnS thin films prepared under various bath temperatures

Bath temperature (°C)	Thickness (nm)
40	97.24
60	104.1
80	123.2

Table 2: Surface roughness values of SnS thin films prepared under various bath temperatures

Bath temperature (°C)	Roughness (nm)
40	5.02
60	10.08
80	12.62

Table 3: Atomic percentage composition of SnS thin films deposited at different chemical bath temperatures from EDAX analysis

Bath temperature (°C)	Elements	Atomic percentage (%)	Sn:S ratio
40	Sn	50.82	1.03
	S	49.18	
60	Sn	50.58	1.02
	S	49.42	
80	Sn	50.09	1.00
	S	49.91	

of the substrate. The grain density observed from AFM images reduced. However, as the bath temperature is increased to 80 °C, these small grains gradually combine and make larger grains (1µm). There are large numbers of Sn and an S ion gets adsorbed on the substrate which leads to

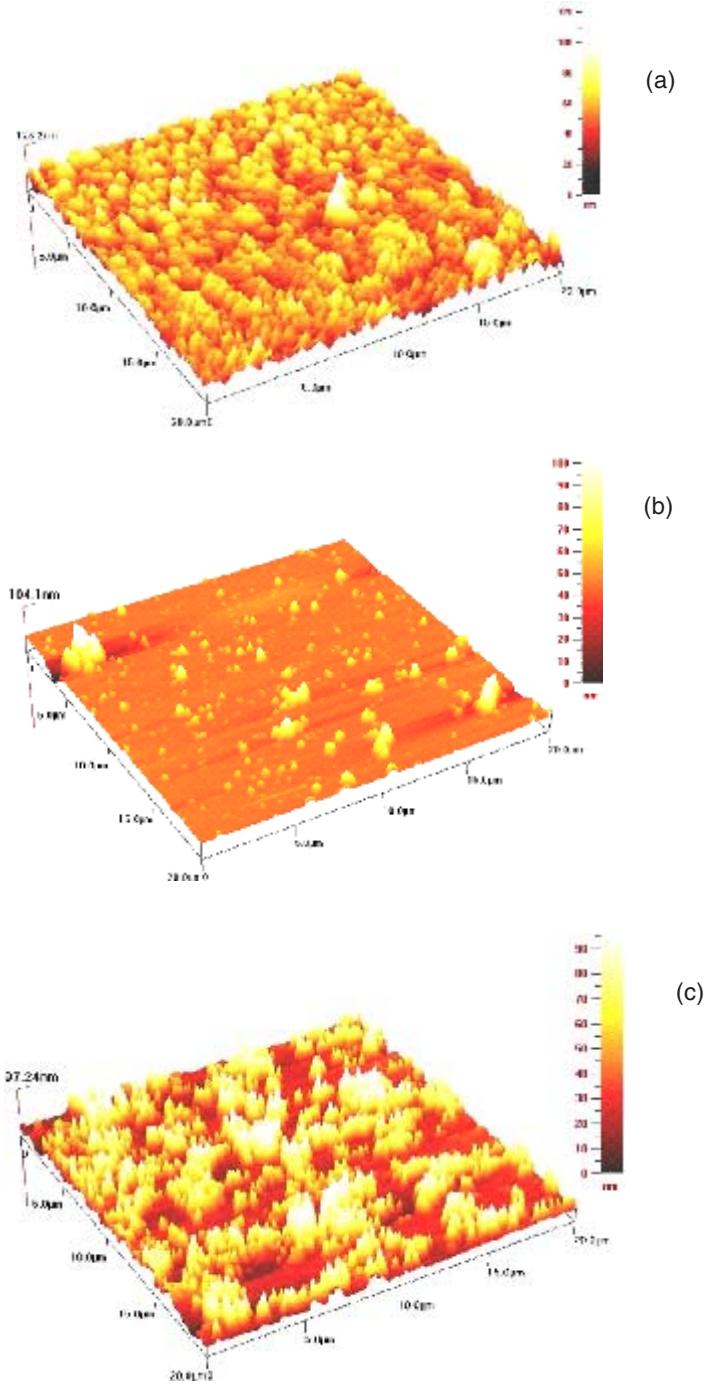

Fig. 1: Atomic force microscopy (AFM) images of SnS films deposited at different chemical bath temperatures. [(a) 80 °C (b) 60 °C (c) 40 °C]

crystallization. These films show a very uniform and complete coverage of material over the surface of substrate.

The study on the influence of bath temperature demonstrates that the thickness (Table 1) and RMS surface roughness (Table 2) increase with bath temperature. The RMS of the roughness was measured to be 5.02 nm for the films prepared at 40 °C. The lowest roughness in films represents the finest particles grown on the microscope glass substrates. It can be seen that the roughness increases with increasing bath temperature up to 80 °C in which the roughness has the highest value (12.62 nm). The surface roughness is unavoidable since grains were grown with different sizes and spherical in shapes.

Figure 2 shows absorbance spectra for the SnS thin films deposited under various bath temperatures. The absorbance is high in the visible region and decrease in the infrared region. The films deposited at the lowest bath temperature (40 °C) show a lower absorption than other samples. This might be due to less SnS thin films deposited onto the surface of substrate providing poor absorption properties. This indicates that 40 °C proved unfavorable towards the films prepared using the current method.

The absorbance data was used to calculate the band gap energy using the Equation 1 (Stern equation).

$$A = \frac{[k\left(hv - E_g\right)^{n/2}]}{hv} \qquad ...(1)$$

where *v* is the frequency, *h* is the Planck's constant, *k* equals a constant while *n* carries the value of either 1 or 4. For direct transition, n=1 and for indirect transition, n=4. Variation of $(Ahv)^2$ versus photon energy (*hv*) shown in Figure 3 (3a, 3b and 3c). The linear nature of the plot reveals that the band gap for SnS films deposited at 40, 60 and 80 °C is 1.5, 1.3, 1.2 eV, respectively. This clearly indicates that the band gap decreases with increase in bath temperature. The band gap values are in good agreement with the values obtained by the other authors[21, 22].

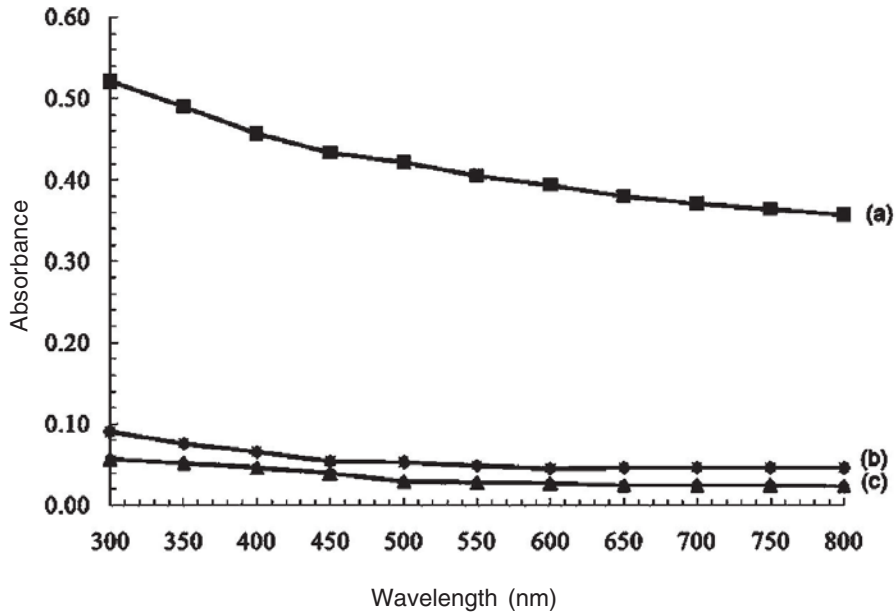

Fig. 2: Optical absorbance versus wavelength of SnS films deposited at different chemical bath temperatures. [(a) 80 °C (b) 60 °C (c) 40 °C]

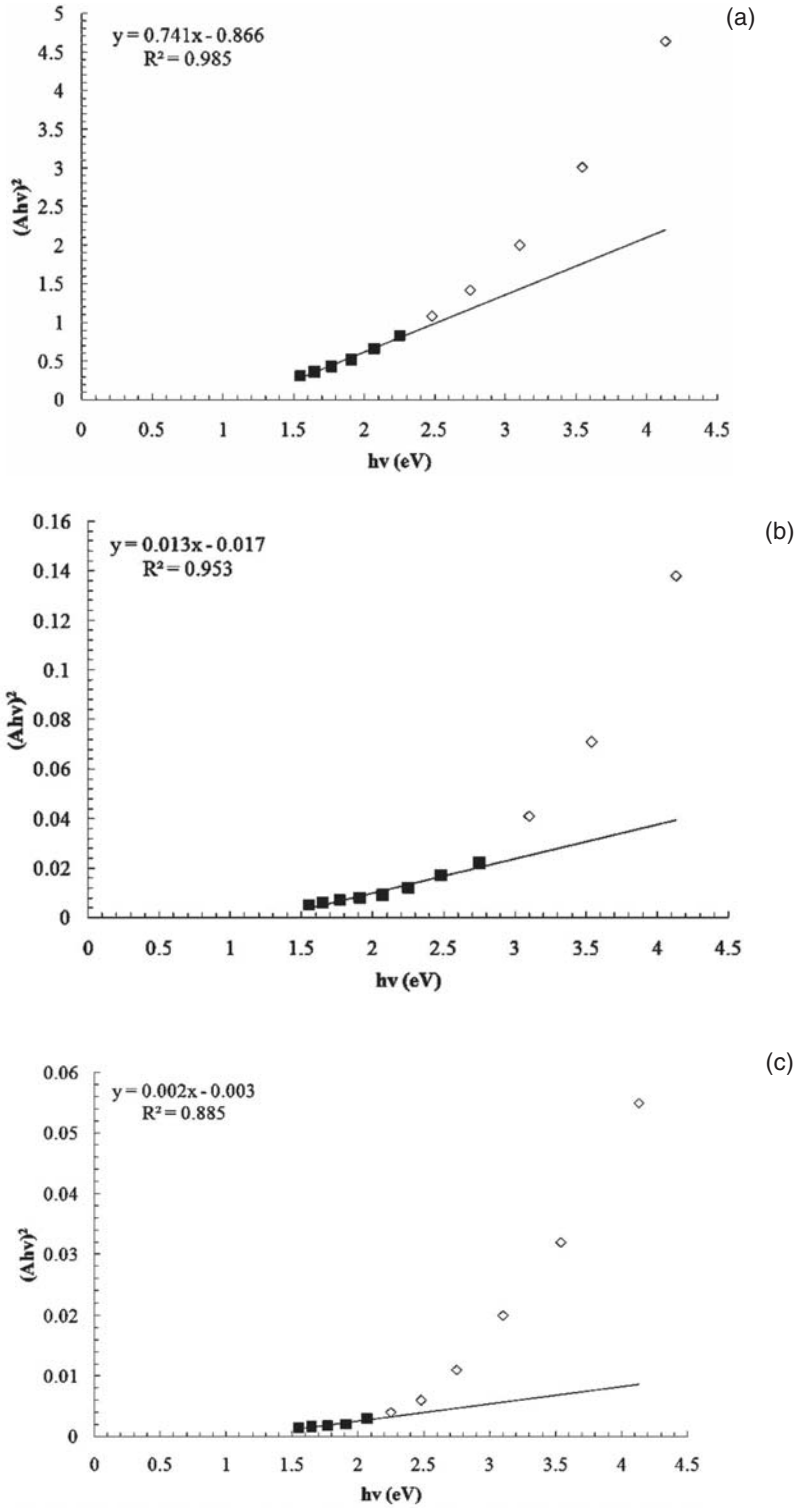

Fig. 3: Plots of (*Ahv*)² versus *hv* of SnS films deposited at different chemical bath temperatures. [(a) 80 °C (b) 60 °C (c) 40 °C]

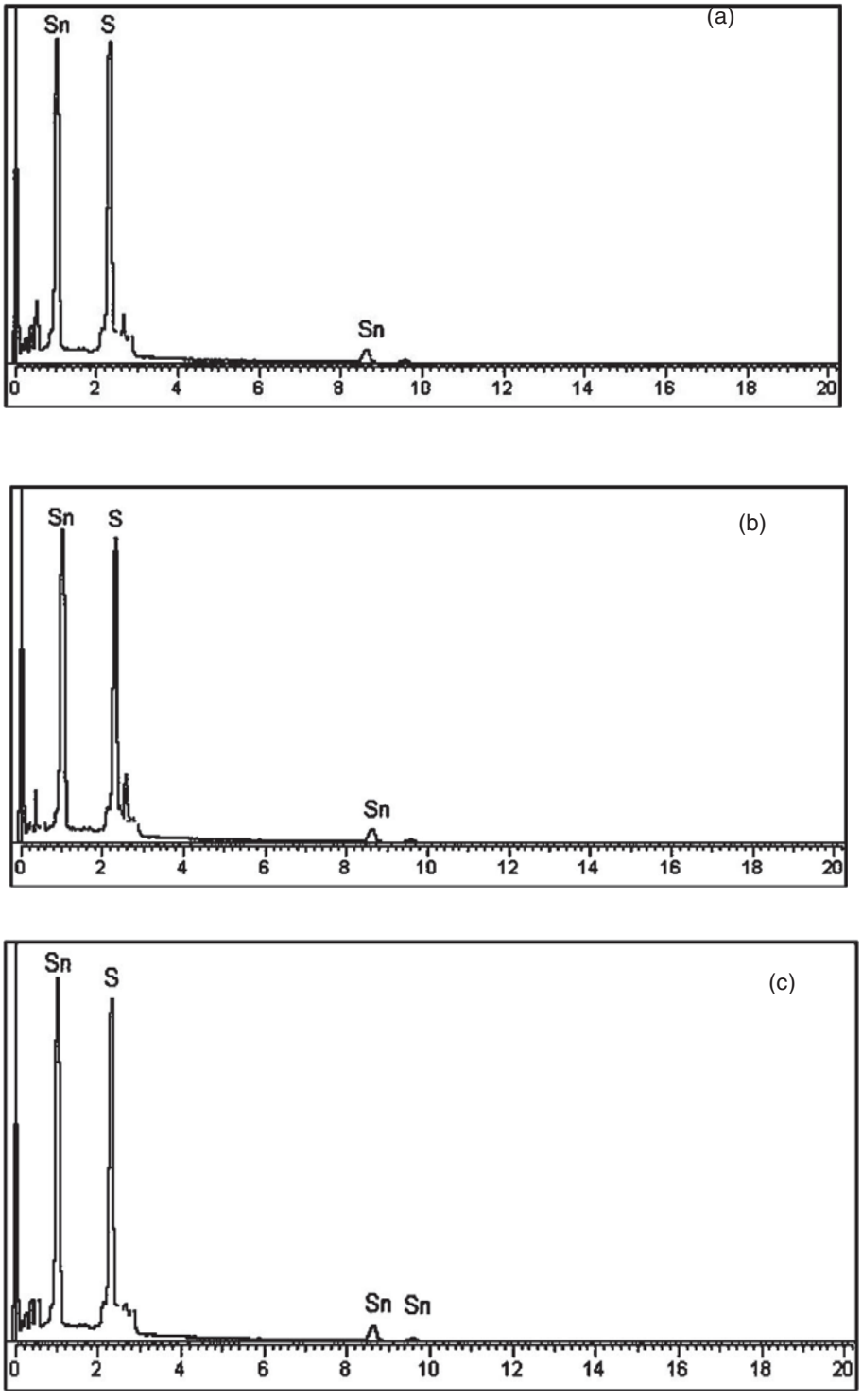

Fig. 4: EDAX spectra of SnS films deposited at different chemical bath temperatures. [(a) 80 °C (b) 60 °C (c) 40 °C]

The films obtained are analyzed by energy dispersive analysis of X-ray (EDAX) technique for checking the stoichiometry of the films. Table 3 shows the ratio of Sn to S from the EDAX results (Figure 4a, 4b and 4c). We can observe that the composition of the films is close to stoichiometry (Sn:S) when the films deposited at 40 (1.03) and 60 °C (1.02). However, the films prepared at 80 °C indicate the formation of a stoichiometry SnS (1:1) deposit.

CONCLUSION

SnS thin films were deposited on microscope glass substrate by chemical bath deposition method. Deposition was carried at different bath temperatures from 40 to 80 °C in the presence of Na_2EDTA as complexing agent. Atomic force microscopy image for the films deposited at 80 °C revealed that all grains uniformly distributed over the surface of substrate indicated well defined growth of SnS material. Optical absorption showed the presence of direct transition and band gap energy decreased from 1.5 to 1.2 eV with the increased of bath temperature from 40 to 80 °C.

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