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Effect of dip time on the structural, electrical and morphological properties of antimony sulphide thin films

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ABSTRACT

Amorphous Sb_2S_3 thin films were deposited on glass substrates by solution growth technique. The structural property was analyzed by XRD, the elemental composition was estimated from EDX analysis while the surface morphology of the film was examined by SEM. The effect of dip time on each of these properties was studied. Amorphous nature of the film was confirmed from XRD and SEM analysis. The thickness of the Sb_2S_3 thin film was estimated from surface profile analysis and found to increase as deposition time increases. The resistance of the films at different dip time was obtained from V/I values from surface profile analysis. The film was seen to have very high resistance in the range of 1.23 x $10^{\circ}\Omega$ to 1.29 x $10^{\circ}\Omega$ while the sheet resistance was in the range of 0.645 x $10^{\circ}\Omega$ -m to 1.23 x $10^{\circ}\Omega$ -m depending on the dip time.

Keywords: Thin films, antimony sulphide, scanning electron microscopy, Surface profile, surface morphology, dip time, solution growth technique, amorphous.

INTRODUCTION

In recent years, there has been an increasing interest in the growth and characterization of metal chalcogenide thin films. This is probably due to the fact that these thin films find applications in photovoltaic devices, optoelectronic and microelectronic devices, anti-reflective (AR) and reflective coatings and so on. Sb_2S_3 is a V-VI binary semiconductor compound which can be represented by the chemical symbol A^vB^{vi} . Chemically deposited Sb_2S_3 thin films are potential absorber materials in devices for photovoltaic conversion of solar energy [1]. Sb_2S_3 also find applications in microwave devices and target materials for television camera. These properties exhibited by Sb_2S_3 make it a good material for thin film deposition. Sb_2S_3 thin films have previously been prepared by different researchers using various techniques such as chemical bath deposition [2-3], vacuum evaporation [4-5], spray pyrolysis [6], etc.

In this research, the solution growth technique (also known as Chemical bath deposition) is preferred as a result of its simplicity. This method offers the advantage of depositing thin films on a large area without using expensive equipments. This process is completely carried out by the addition of a suitable complexing agent. The essence of the complexing agent is to slow down the release of the metal ions on dissociation, thus resulting in slow precipitation of the compound in the chemical bath by ion-ion reaction. The thin film then forms on the substrate as well as on the sides of the chemical bath by this method.

In this research, thin films of Sb_2S_3 were deposited on glass substrates from an acidic medium containing 5ml of 1.0M of SbCl₃, 2ml of TEA, 5ml of 1.0M of Na₂S₂O₃ and 38ml of pure laboratory distilled water to make up the

50ml mark of the beaker used. The surface morphology and elemental composition of the films were obtained using a Carl Zeiss MA-10 scanning electron microscope with EDX, the thickness of the films was obtained using a Dektak Veeco 7.0 surface profiler while the structural analysis was done using a PAnalytical X'Pert Pro MPD XRD respectively.

MATERIALS AND METHODS

2.1. Materials

All the chemicals used for the deposition process were analytical grade. They include antimony tri-chloride (SbCl₃), tri-ethanolamine (TEA) and sodium thiosulphate (Na₂S₂O₃) respectively. During the deposition process, SbCl₃ served as the source of Sb³⁺, TEA was used as a complexing agent while Na₂S₂O₃ acted as the source of sulphide ion (S²⁻). The dimension of the glass substrate used is 76mm x 26mm x 1mm. These microscopic glass slides were soaked in detergent for 48hrs and rinsed thoroughly in distilled water and allowed to dry in open air prior to deposition of the films.

2.2. Experimental Procedure

5ml of 1.0M of SbCl₃ was put into a 50ml beaker followed by the addition of 2ml of TEA. The resulting mixture was stirred continuously until a clear homogeneous solution was obtained. 5ml of 1.0M of $Na_2S_2O_3$ was added to the mixture which was again stirred with a glass rod stirrer for about 2mins to allow for evenly mixture of the chemicals. 38ml of distilled water was added to the reaction bath to make up 50ml. The overall solution was again stirred continuously to ensure homogeneity of the solution. The pH of the resulting solution was found to be 2.23. The clean microscopic glass slide was clamped vertically into the solution through a synthetic foam cover. The cover was necessary in order to prevent dust or unwanted particles from entering the solution while the clamp was necessary to prevent the substrate from shaking during deposition. After about 15mins, the transparent solution became yellowish-orange indicating the initiation of a chemical reaction. The deposition was carried out using four different 50ml beakers in which deposition time was removed from the solution, rinsed well with distilled water and allowed to dry in open air for about 2hours. The coated micro-slides were later placed in an air-tight box to prevent them from coming in contact with dirt and moisture and kept for further characterization. The deposition process was allowed to proceed at room temperature (~ 300K). The process involved in the deposition of Sb₂S₃ thin films has been suggested by the authors as follows:

 $SbCl_3 + TEA \rightarrow [Sb(TEA)]^{3+} + 3Cl^{-1}$

 $[Sb(TEA)]^{3+} \rightarrow Sb^{3+} + TEA$

Sodium thiosulphate will dissociate in the acidic medium to form the complex according to the reaction:

$$Na_2S_2O_3 \rightarrow S_2O_3^{2-} + 2Na$$

In acidic medium, sulphide ions can be gradually released from the thiosulphate ions upon hydrolytic decomposition according to the reaction:

$$S_2O_3^{2-} + H^+ \rightarrow S + HSO_3^{--}$$

 $S + 2e^{-} \rightarrow S^{2-}$

The sulphide ion released then combines with the antimony (III) ion released from the TEA complex and condenses on the glass substrate to form yellow-orange Sb_2S_3 :

 $2Sb^{3\scriptscriptstyle +}+3S^{2\scriptscriptstyle -} {\rightarrow} Sb_2S_3 \downarrow$

RESULTS AND DISCUSSION

3.1 Thickness Variation of the Sb₂S₃ Thin Films

The thickness of the films grown in this research increases from 0.5µm to 1.0µm as dip time increases from 12hrs to 48hrs as shown in figure 1.1.



Fig. 1.1: Variation of thickness of as-deposited Sb₂S₃ thin films with dip time.

3.2 Surface Profile of the Films

The surface profile of the Sb_2S_3 thin films for different dip time are displayed in figure 1.2 (a-d) below.



Fig. 1.2a: Surface profile of the Sb₂S₃ thin film obtained at 12hr dip time.



Fig. 1.2b: Surface profile of the Sb₂S₃ thin film obtained at 24hr dip time.



Fig. 1.2c: Surface profile of the Sb₂S₃ thin film obtained at 36hr dip time.



Fig. 1.2d: Surface profile of the Sb₂S₃ thin film obtained at 48hr dip time.

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3.3. Structural Characterization

The structural property of the as-deposited Sb_2S_3 thin films was investigated by means of x-ray diffraction (XRD) using an X'PERT PRO diffractometer with CuK α radiation ($\lambda = 1.54060$ Å). The accelerating voltage and current were respectively 40kV and 30mA with values of 2 θ in the range of 0° to 80° at a measurement temperature of 25°C. The Sb₂S₃ thin films were scanned continuously between 0° and 80° at a step size of 0.004 and at a time per step of 3.175 secs.

Typical diffraction patterns of Sb_2S_3 thin films are shown in figure 1.3 (a, b & c). Sharp XRD peaks are not observed for the as-deposited Sb_2S_3 thin films. All the films deposited at room temperature show amorphous nature. From the results obtained in this research, we deduce that even though dip time was increased, there was no significant change in the structure of the film. This implies that dip time has little or no effect on the structure of the films deposited at room temperature. This is an indication that the as-deposited Sb_2S_3 thin films are of poor crystalline nature and are thus amorphous. The amorphous nature of the as-deposited Sb_2S_3 thin films have previously been reported [7-10].





Fig. 1.3a: XRD spectra of as-deposited Sb₂S₃ thin films at 12hr dip time.

Fig. 1.3b XRD spectra of as-deposited Sb₂S₃ thin films at 24hr dip time.



Fig. 1.3c: XRD spectra of as-deposited Sb₂S₃ thin films at 36hr dip time.

3.4. Morphological Studies

The morphological characteristics of the as-deposited Sb_2S_3 thin films were studied by scanning electron microscopy (SEM).

The SEM micrographs of the chemically deposited Sb_2S_3 thin films are shown in figure 1.4 (a & b) for two different dip time (12hrs & 24hrs). The micrographs of Sb_2S_3 deposited at 12hr dip time show a cluster of spheres which are irregularly distributed over the surface of the film. We see clearly from figure 1.4 (a & b) that there are fewer cluster of spheres in 1.4b which appear to be larger than those formed in figure 1.4a. This trend is likely to continue at higher dip time. This, we believe, is an indication of overgrowth of the particles which imply an increase in thickness of the as-deposited Sb_2S_3 thin films as dip time increases. From the SEM micrographs obtained in this research, it is obvious that the thickness of the as-deposited Sb_2S_3 thin films increases with an increase in dip time. Figure 1.4 (a & b) are shown below.



Fig. 1.4a: SEM micrograph of as-deposited Sb₂S₃ thin films deposited at 12hrs dip time.



Fig. 1.4b: SEM micrograph of as-deposited Sb₂S₃ thin films deposited at 24hrs dip time.

3.5 Electrical Studies

The electrical property studied is the film resistance and sheet resistance. The film resistance, R_x and sheet resistance, R_s of this material was calculated from V/I values given by the surface profiler. The film resistance was calculated using the expression:

 $R_x = KV/I$

where K is a constant equal to 4.523.

The sheet resistance R_s of the material was calculated using the expression:

 $\mathbf{R}_{s} = \mathbf{R}_{x}\mathbf{t}$

where t is the thickness of the film.

The values of the film resistance, sheet resistance, V/I values and thickness of the films obtained at different dip time are presented in table 1.

$R_x (x 10^9 \Omega)$	V/I (x 10 ⁸)	Time (Hrs)	Thickness (µm)	$R_s (x 10^3 \Omega - m)$
1.29	2.84	12	0.5	0.645
1.27	2.81	24	0.7	0.889
1.24	2.75	36	0.75	0.930
1.23	2.72	48	1.0	1.23

Table 1. Electrical properties for 50203 thin thins obtained at unterent dip thile and the knew	Table 1: Electrical	properties for	Sb ₂ S ₃ thin fill	ms obtained at	different dig	o time and thickness.
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From table 1, it is observed that the all the films deposited in this research have very high resistance in the range of $1.23 \times 10^{9}\Omega$ to $1.29 \times 10^{9}\Omega$ respectively depending on the dip time and film thickness. From the table, it is obvious that dip time has a considerable effect on the resistance of the films since the film resistance is seen to decrease with a corresponding increase in dip time. Thus we see that the film has the highest resistance at the lowest dip time while the resistance is low at a higher dip time respectively.

The sheet resistance of the material is seen to increase with a corresponding increase in dip time and thickness of the films grown in this research. The sheet resistance of the material is in the range of 0.645 x $10^{3}\Omega$ -m to $1.23 \times 10^{3}\Omega$ -m depending on the dip time.

3.6. Energy-Dispersive Analysis Spectrum

The elemental composition and chemical states of the films under study was analyzed by Energy-dispersive analysis x-ray spectroscopy (EDAX).

In the EDX spectrum of Sb_2S_3 films, the presence of Sb, Cl and S are observed as displayed in figure 1.5 (a & b). The atomic percentage of Sb increases from 1.39% to 5.15% as dip time increased from 12hrs to 24hrs respectively

while the atomic percentage of S show an increment from 1.42% to 4.81% as dip time increased from 12hrs to 24hrs. The results obtained indicate that the films are non-stoichiometric. The oxygen peak detected from the EDX spectrum is unavoidable in any chemically deposited films as previously reported [11]. The presence of Cl in the EDX spectrum is due to the precursor SbCl₃ while the presence of Na is due to the precursor Na₂S₂O₃. The other elements present may have come from the glass slide and reagents used. Figure 1.5 (a & b) are shown below.



dip time.



CONCLUSION

Thin films of Sb_2S_3 were successfully deposited on glass substrates at room temperature. Morphological studies, compositional analysis and x-ray diffraction measurements were successfully carried out on the films. The effect of dip time on the structural, morphological, electrical and elemental compositional properties was studied. Results show that an increase in dip time has a considerable effect on thickness of the film, morphology, electrical and elemental compositional characteristics. However, it was observed from XRD result that an increase in dip time has no effect on the structure of the films deposited in this research, as all the films grown at different dip time show amorphous nature. The thickness of the films deposited in this work was between 0.5 μ m and 1.0 μ m depending on the dip time.

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