Electrical and morphological study of thermally evaporated \((\text{Sb}_2\text{S}_3)_{1-x}\text{Sn}_x\) thin films

Bushra A. Hasan, Hiba H. Issa

Department of Physics, College of Science, University of Baghdad

E-mail: Bushra_abhasan@yahoo.com

Abstract

\((\text{Sb}_2\text{S}_3)_{1-x}\text{Sn}_x\) thin films with different concentrations (0, 0.05 and 0.15) and thicknesses (300, 500 and 700nm) have been deposited by single source vacuum thermal evaporation onto glass substrates at ambient temperature to study the effect of tin content, thickness and on its structural morphology, and electrical properties. AFM study revealed that microstructure parameters such as crystallite size, and roughness found to depend upon deposition conditions. The DC conductivity of the vacuum evaporated \((\text{Sb}_2\text{S}_3)_{1-x}\text{Sn}_x\) thin films was measured in the temperature range (293-473)K and was found to increase on order of magnitude with increase of thickness, and tin content. The plot of conductivity with reciprocal temperature suggests, there are three activation energies \(E_a1, E_a2\) and \(E_a3\) for \((\text{Sb}_2\text{S}_3)_{1-x}\text{Sn}_x\) for all \(x\) content values and thicknesses which decreases with increasing tin content and thickness. Hall effect measurement showed that low thickness \((\text{Sb}_2\text{S}_3)_{1-x}\text{Sn}_x\) film exhibit n-type conductance whereas the film exhibit p-type towards the higher thickness. The electric carrier concentration and mobility show opposite dependence upon tin content and thickness.

Key words

\((\text{Sb}_2\text{S}_3)_{1-x}\text{Sn}_x, \text{thin films}, \text{D.C. Hall effect.}\)

Article info.

Received: Aug. 2014
Accepted: Dec. 2014
Published: Apr. 2015

\(\text{Sb}_2\text{S}_3\) \(\text{Sn}_x\) 

(\(\text{Sb}_2\text{S}_3\) \(\text{Sn}_x\) 

Electrical and morphological study of thermally evaporated \((\text{Sb}_2\text{S}_3)_{1-x}\text{Sn}_x\) thin films

Bushra A. Hasan, Hiba H. Issa

Department of Physics, College of Science, University of Baghdad

E-mail: Bushra_abhasan@yahoo.com

Abstract

\((\text{Sb}_2\text{S}_3)_{1-x}\text{Sn}_x\) thin films with different concentrations (0, 0.05 and 0.15) and thicknesses (300, 500 and 700nm) have been deposited by single source vacuum thermal evaporation onto glass substrates at ambient temperature to study the effect of tin content, thickness and on its structural morphology, and electrical properties. AFM study revealed that microstructure parameters such as crystallite size, and roughness found to depend upon deposition conditions. The DC conductivity of the vacuum evaporated \((\text{Sb}_2\text{S}_3)_{1-x}\text{Sn}_x\) thin films was measured in the temperature range (293-473)K and was found to increase on order of magnitude with increase of thickness, and tin content. The plot of conductivity with reciprocal temperature suggests, there are three activation energies \(E_a1, E_a2\) and \(E_a3\) for \((\text{Sb}_2\text{S}_3)_{1-x}\text{Sn}_x\) for all \(x\) content values and thicknesses which decreases with increasing tin content and thickness. Hall effect measurement showed that low thickness \((\text{Sb}_2\text{S}_3)_{1-x}\text{Sn}_x\) film exhibit n-type conductance whereas the film exhibit p-type towards the higher thickness. The electric carrier concentration and mobility show opposite dependence upon tin content and thickness.
**Introduction**

Antimony Sulphide is a semiconducting chalcogenide of the VIB and VIIB groups of elements. Due to its attractive photo conducting properties and high thermoelectric power, \(\text{Sb}_2\text{S}_3\) has wide industrial applications such as target material in television camera, microwave devices, switching devices and optoelectronic devices [1-4]. With an optical band gap in the range of 1.06 eV to 1.88 eV in crystals and in polycrystalline thin films with \(V_2\text{-VI}_3\) composition [5, 6], the sulfides and selenides of antimony are potential absorber materials in devices for photovoltaic conversion of solar energy. The electrical property of semiconductors depends on the chemical composition and the structural features. Dielectric measurements of amorphous chalcogenide semiconductors have been used to understand the conduction process in these materials.

**Experimental details**

The compounds of \((\text{Sb}_2\text{S}_3)_{1-x} \text{Sn}_x\) were prepared by quenching technique. The exact amount of high purity (99.999%) (\(\text{Sb, S}\) and \(\text{Sn}\)) elements accordance with their atomic percentages were weighed using an electronic balance with the least count of \((10^{-4} \text{ gm})\). The mixed elements were sealed in evacuated (~\(10^{-3}\) Torr) quartz ampoule (length ~ 25 cm and internal diameter ~ 8 mm). The ampoules which containing the elements were heated to 1273K for 20 hours then cooled to room temperature. The temperature of the furnace was raised at a rate of 100°C/min. During heating the ampoules are constantly rocked. This is done to obtain homogeneous compounds. Amorphous \((\text{Sb}_2\text{S}_3)_{1-x} \text{Sn}_x\) thin films with \((x= 0, 0.05\) and 0.15\) of different thickness \((t= 300, 500\) and 700\) nm were prepared using thermal evaporation by continuously feeding the material with a powder to a heated molybdenum boat of melting point about 2895K at which temperature instantaneous evaporation of the material takes place. Corning glass slides substrates were used, and the distance of the source to substrate was 15 cm. The evaporation carried out using Edward coating unit (model E306A). During the evaporation of the films, the pressure in the system was \(4\times10^{-5}\) Torr. All the samples were prepared under constant condition (pressure, rate of deposition (3nm/sec), substrate temperature (room temperature)). To study the electrical properties for the films Ohmic contacts for the prepared films are produced by evaporating (Al) electrodes of 300 nm thickness, by means of thermal evaporation methods. Then the d.c conductivity \((\sigma)\) has been studied using the electrical circuit which is consists of oven type Herease and keithley (616). The thickness of the prepared films has been determined using Fizeau fringes of equal thickness are obtained in an optical aperture. The film thickness \((t)\) is given by:

\[
t = \frac{\lambda \Delta x}{2 x}
\]

where \(\Delta x\) is the shift between the interference fringes, \(x\) is the distance between the interference fringes and \(\lambda\) is the He: Ne wavelength (589.3 nm).

XRD of the prepared \((\text{Sb}_2\text{S}_3)_{1-x} \text{Sn}_x\) films revealed no diffraction peaks, i.e. the structures was amorphous espied of increase of tin content and thickness. The composition investigation of the \((\text{Sb}_2\text{S}_3)_{1-x} \text{Sn}_x\) alloys with different tin content showed the ratio of \((\text{Sb} – \text{S} – \text{Sn})\) as 41 – 59, 38 – 55.75 – 6.25, and 34 – 50.14 – 15.86 respectively.

**Results and discussion**

Figs.1-3 show three dimensional AFM images of \((\text{Sb}_2\text{S}_3)_{1-x} \text{Sn}_x\) thin films grown with different tin content having thickness...
300, 500, 700 nm. Two-dimensional grain size of (Sb₂S₃)₁₋ₓ Snₓ thin films were measured by using nano scale reading. As it can be seen from this figure, the film is composed of small particles of average grain size between (80 and 110) nm. It is obvious from table 1 that the average grain size get to decreases with increase of Sn content and thickness, indeed the grain size decreases from 110.46 to 91.42 nm, from 101.67 to 86.70 nm and from 92.66 to 81.31 nm for t = 300, 500 and 700 nm respectively when Sn content increases from 0 to 0.15. On the other hand the results showed that average roughness increased with thickness at low Sn ratio and then become constant (thickness independent) at high Sn ratio, indeed average roughness increases from 0.125 to 0.31 when t increases from 300 to 700 nm at Sn content 0.05.

![AFM pictures for (Sb₂S₃)₁₋ₓ Snₓ films 300 nm in thickness with different Sn contents (x=0, 0.05 and 0.15).](image)

Fig. 1: AFM pictures for (Sb₂S₃)₁₋ₓ Snₓ films 300 nm in thickness with different Sn contents (x=0, 0.05 and 0.15).
Fig. 2: AFM pictures for (Sb₂S₃)₁₋ₓSnₓ films 500 nm in thickness with different Sn contents (x=0, 0.05 and 0.15).
Fig. 3: AFM pictures for (Sb$_2$S$_3$)$_{1-x}$Sn$_x$ films 700 nm in thickness with different Sn contents ($x=0$, 0.05 and 0.15).
Table1: Average grain size and average roughness for (Sb$_2$S$_3$)$_{1-x}$Sn$_x$ films with different Sn content at different substrate Thickness.

| t (nm) | Sn content | Average grain size (nm) | Average roughness (nm) |
|-------|------------|-------------------------|------------------------|
| 300   | 0          | 110.46                  | 0.195                  |
|       | 0.05       | 106.54                  | 0.125                  |
|       | 0.15       | 91.42                   | 0.135                  |
| 500   | 0          | 101.67                  | 0.0338                 |
|       | 0.05       | 89.48                   | 0.24                   |
|       | 0.15       | 86.70                   | 0.136                  |
| 700   | 0          | 92.66                   | 0.122                  |
|       | 0.05       | 81.94                   | 0.31                   |
|       | 0.15       | 81.31                   | 0.134                  |

Fig.4 represents the variation of conductivity versus inverse of absolute temperature with various tin content and thicknesses for (Sb$_2$S$_3$)$_{1-x}$ Sn$_x$ films. It is observed that conductivity increases with increase in temperature. It is inferred that film material behaves as semi conducting at hole temperature range. For all the films, conductivity follows the relation

$$\sigma = \sigma_0 \exp(-\frac{E_a}{k_B T})$$

(2)

where $\sigma$ is conductivity at temperature T, $\sigma_0$ is constant, $k_B$ is the Boltzmann constant and $E_a$ is the activation energy. It is clear from these figures that there are three activation energy and hence three transport mechanism for (Sb$_2$S$_3$)$_{1-x}$Sn$_x$ with different Sn content (x = 0, 0.05 and 0.15). According to Davis and Mott model 1979[7] the tails of localized states should be rather narrow and extend a few length of tenths of an electron volt into the forbidden gap, and further more thus suggested of localized levels near the middle of the gap. This leads to three basically different channels of conduction: $E_{a1}$ is the activation energy required to transport electron from Fermi level to the extended states above the conduction band edge $E_c$, $E_{a2}$ is the activation energy required to transport electron from Fermi level to the localized below the conduction band edge, and $E_{a3}$ is the activation energy required to transport electron between localized states at Fermi level.
Fig. 4: The relation between $\ln(\sigma)$ versus reciprocal of temperature for $(Sb_2S_3)_{1-x}Sn_x$ films with different Sn content and thicknesses.
The increasing of thickness has no effect of the number on transport mechanisms of the system (Sb$_2$S$_3$)$_{1-x}$Sn$_x$. The variation of $E_a$ for as-deposited (Sb$_2$S$_3$)$_{1-x}$Sn$_x$ thin films with thickness and tin content are given in Table 2. It is clear from this table that the activation energies decrease with the increase of film thickness and Sn content. Indeed $E_{a1}$ decreases from 0.5412 to 0.3292 eV when the thickness increases from 300 nm to 700 nm at $x=0$, while, also $E_{a1}$ decreases from 0.5412 to 0.1923 eV with the increase of tin content from 0 to 0.15. The decreasing of the activation energies with increasing of tin content may be due to the local ordering structure of the Sb$_2$S$_3$. The addition of tin to the binary system at highest contents leads to creation of defect states, resulting in an increase of the electron density in the conduction band, while the decreasing of activation energy $E_{a1}$ with the increase of thickness is resulting from the effect of reduction of energy gap and in turn reduces the energy requires to transport the carriers from Fermi level to the conduction band. The impurities, voids and defects present in the film are removed when thickness increased while they created more and more by the effect of tin constant.

| t (nm) | X | $E_{a1}$ (eV) | Temp.Range (K) | $E_{a2}$ (eV) | Temp.Range (K) | $E_{a3}$ (eV) | Temp.Range (K) | $\sigma_{RT} \times 10^{-5}$ (Ω.cm)$^{-1}$ |
|-------|---|-------------|----------------|-------------|----------------|-------------|----------------|----------------------------------|
| 300   | 0 | 0.0185      | 293-393        | 0.1389      | 403-433        | 0.5412      | 443-473        | 0.105                            |
|       | 0.05 | 0.0146      | 293-363        | 0.0853      | 373-423        | 0.2373      | 433-473        | 0.133                            |
|       | 0.15 | 0.0182      | 293-343        | 0.0363      | 353-423        | 0.1923      | 433-473        | 0.669                            |
| 500   | 0 | 0.0129      | 293-373        | 0.1353      | 383-423        | 0.4082      | 433-473        | 0.133                            |
|       | 0.05 | 0.0098      | 293-353        | 0.1305      | 363-413        | 0.2337      | 423-473        | 0.156                            |
|       | 0.15 | 0.0058      | 293-323        | 0.0122      | 333-403        | 0.1345      | 423-473        | 0.902                            |
| 700   | 0 | 0.0179      | 293-333        | 0.1310      | 343-403        | 0.3292      | 413-473        | 0.228                            |
|       | 0.05 | 0.0160      | 293-343        | 0.1223      | 343-423        | 0.1612      | 423-473        | 0.529                            |
|       | 0.15 | 0.0075      | 293-333        | 0.0177      | 343-413        | 0.2613      | 433-473        | 1.111                            |

Hall effect phenomena is used as mentioned previously to determine the type of the majority charge carriers, concentration ($n_H$) and Hall mobility ($\mu_H$) for (Sb$_2$S$_3$)$_{1-x}$Sn$_x$ thin films deposited at room temperature with different thicknesses (300, 500 and 700) nm and Sn content. The coefficient of Hall ($R_H$) were calculated and listed in Table 3. It is clear from this table that the samples at $x=0.05$ and $x=0.15$ with thickness $t=300$ nm have a negative Hall coefficient (n-type), i.e. Hall voltage decreases with the increase of the current. It is well established fact that (Sb$_2$S$_3$)$_{1-x}$Sn$_x$ film exhibit n-type conductivity and this n-type conduction is generally attributed to free electrons from donor levels of sulfide [8]. The density of this donor sulfide decreases as thickness increases. Hence the increase in conductivity is probably due to decrease of energy gap of the film which is in good agreement with the earlier results reported in this paper.
Table.3: Hall Effect measurements for (Sb$_2$S$_3$)$_{1-x}$Sn$_x$ film with different thicknesses and Sn content.

| t (nm) | x  | R$_H$ (cm$^3$/C)*10$^7$ | n$_H$ (cm$^{-3}$)*10$^{11}$ | type | $\mu$$_H$ (cm$^2$/V.sec) |
|--------|----|----------------------|----------------------------|------|---------------------|
| 300    | 0  | -1.35                | 1.57                       | n    | 66.92               |
|        | 0.05 | 3.82                | 2.54                       | p    | 50.81               |
|        | 0.15 | -10.03              | 2.67                       | n    | 40.65               |
| 500    | 0  | 3.18                 | 2.55                       | p    | 42.29               |
|        | 0.05 | 3.04                | 2.74                       | p    | 33.92               |
|        | 0.15 | 2.68                | 10.13                      | p    | 30.97               |
| 700    | 0  | 2.17                 | 3.79                       | p    | 39.16               |
|        | 0.05 | 4.51                | 4.24                       | p    | 23.85               |
|        | 0.15 | 0.53                | 11.79                      | p    | 8.44                |

Conclusions
There are three conduction mechanisms throughout the D.C conductivity take place in (Sb$_2$S$_3$)$_{1-x}$Sn$_x$ for low thickness and tin content. Increase of thickness improved the structure of the prepared thin films.

References
[1] K. Li, F. Huang, X. Lin, Scripta Mater, 58 (2008) 834.
[2] Q. Han, L. Chen, M. Wang, X. Yang, L. Lu, X. Wang, Mater Sci Eng, 166 (2010) 118.
[3] M. Sun, D. Li, W. Li, Y. Chen, Z. Chen, Y. He, X. Fu, J Phys Chem C. 112 (2008) 18076.
[4] X. Cao, L. Gu, L. Zhuge, W. Gao, W. Wang, S. Wu, Adv Funct Mater, 16 (2006) 896.
[5] F. Aousgi, M. Kanzari, Journal of Optoelectronics and Advanced materials, 12, 6 (2010) 227.
[6] T. Nair, Y. Pena, J. Campos, V. Garica, P. Nair, J. Electrochem. Soc. 145, 8 (1998) 2113.
[7] N. Mott, E. Davis "Electronic Process in Non-crystalline Materials", 2nd ed., University Press, Oxford P.858 (1979).
[8] S. M. Sze, "Physics of semiconductor Devices", Wiley, New York, 1981, 751-849.