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Electrical and morphological study of thermally evaporated $(Sb_2S_3)_{1-x}Sn_x$ thin films

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Abstract

$(Sb_2S_3)_{1-x}Sn_x$ 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 $(Sb_2S_3)_{1-x}$ 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 Ea_1, Ea_2 and Ea_3 for $(Sb_2S_3)_{1-x}$ Sn_x for all x content values and thicknesses which decreases with increasing tin content and thickness. Hall effect measurement showed that low thickness $(Sb_2S_3)_{1-x}$ 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
$(Sb_2S_3)_{1-x}$ Sn_x thin films, D.C, uHall effect.

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دراسة كهربائية وتركيبية لاغشية $(Sb_2S_3)_{1-x}Sn_x$ الرقيقة المحضرة بالتبخير الحراري

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الخلاصـة

حضرت أغشية رقيقة من $(Sb_2S_3)_{1-x}Sn_x$ لنسب مختلفة من محتوى القصدير (0، 0.05، 0.15) وبأسماك 500 (700nm and 300,)باستخدام التبخير الحراري ومن مصدر واحد على أرضيات الزجاج وعند درجة حرارة الغرفة لدراسة تأثير محتوى القصدير على الخواص التركيبية والكهربائية. أظهرت قياسات AFM أن معلمات التركيب الدقيق مثل معدل الحجم الحبيبي وخشونة السطح يعتمد على ظروف التحضير. التوصيلية الكهربائية المستمرة والتي تم قاسها عند مدى درجات الحرارة K(473-293) وجد أنها ازدادت مرتبة واحدة مع زيادة محتوى القصدير والسمك. رسم العلاقة بين التوصيلية الكهربائية المستمرة ومقلوب درجة الحرارة يظهر ان هناك ثلاث طاقات للتنشيط Ea_1، Ea_2, Ea_3 لأغشية $(Sb_2S_3)_{1-x}$ Sn_x لجميع قيم محتوى القصدير والسمك. بينت قياسات تأثير هول أن أغشية $(Sb_2S_3)_{1-x}$ Sn_x ذات السمك الواطئ تظهر توصيلية النوع السالب بينما تظهر الأغشية ذات السمك العالي تظهر توصيلية النوع الموجب. تركيز الحاملات الشحنة والتحركية اظهرا اعتمادا معاكسا مع زيادة قيمة محتوى محتوى القصدير والسمك.

Introduction

Antimony Sulphide is a semiconducting chalcogenide of the V^B and V^{IB} groups of elements. Due to its attractive photo conducting properties and high thermoelectric power, Sb_2S_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 policrystalline thin films with V_2-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 $(Sb_2S_3)_{1-x}$ Sn_x were prepared by quenching technique. The exact amount of high purity (99.999%) (Sb,S and Sn) elements accordance with their atomic percentages were weighed using an electronic balance with the least count of (10^{-4} 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 of10oC/min. During heating the ampoules are constantly rocked .This is done to obtain homogeneous compounds. Amorphous $(Sb_2S_3)_{1-x}$ 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 $4x10^{-5}$ 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 (σ) 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:

$$t = \frac{\lambda}{2}\frac{\Delta x}{x} \qquad (1)$$

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

XRD of the prepared $(Sb_2S_3)_{1-x}$ 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 $(Sb_2S_3)_{1-x}$ Sn_x alloys with different tin content showed the ratio of (Sb – S – 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 $(Sb_2S_3)_{1-x}$ Sn_x thin films grown with different tin content having thickness

300,500,700nm. Two-dimensional grain size of $(Sb_2S_3)_{1-x}$ Sn_x 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.

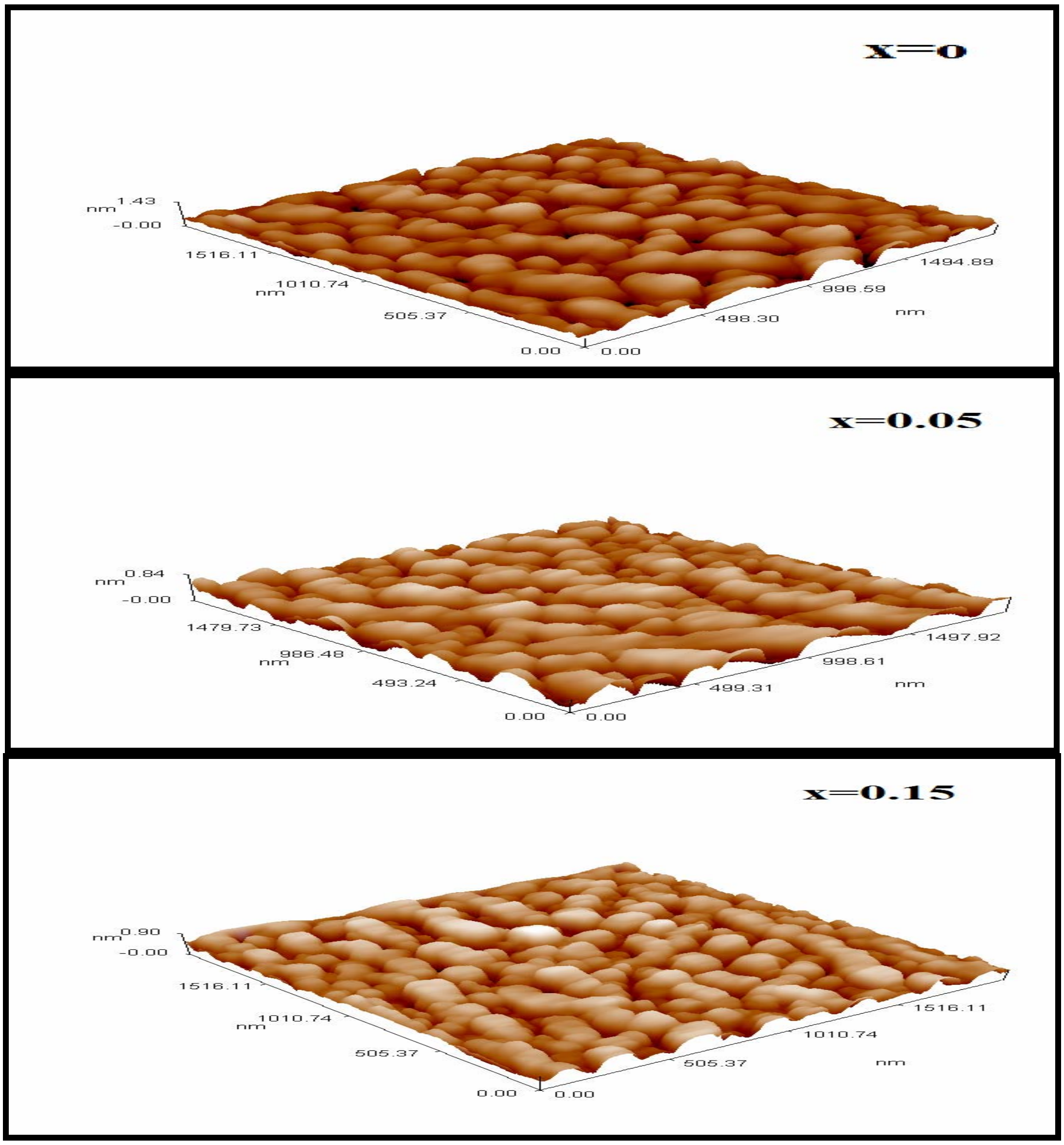

Fig. 1: AFM pictures for $(Sb_2S_3)_{1-x}Sn_x$ films 300 nm in thickness with different Sn contents (x=0, 0.05 and 0.15).

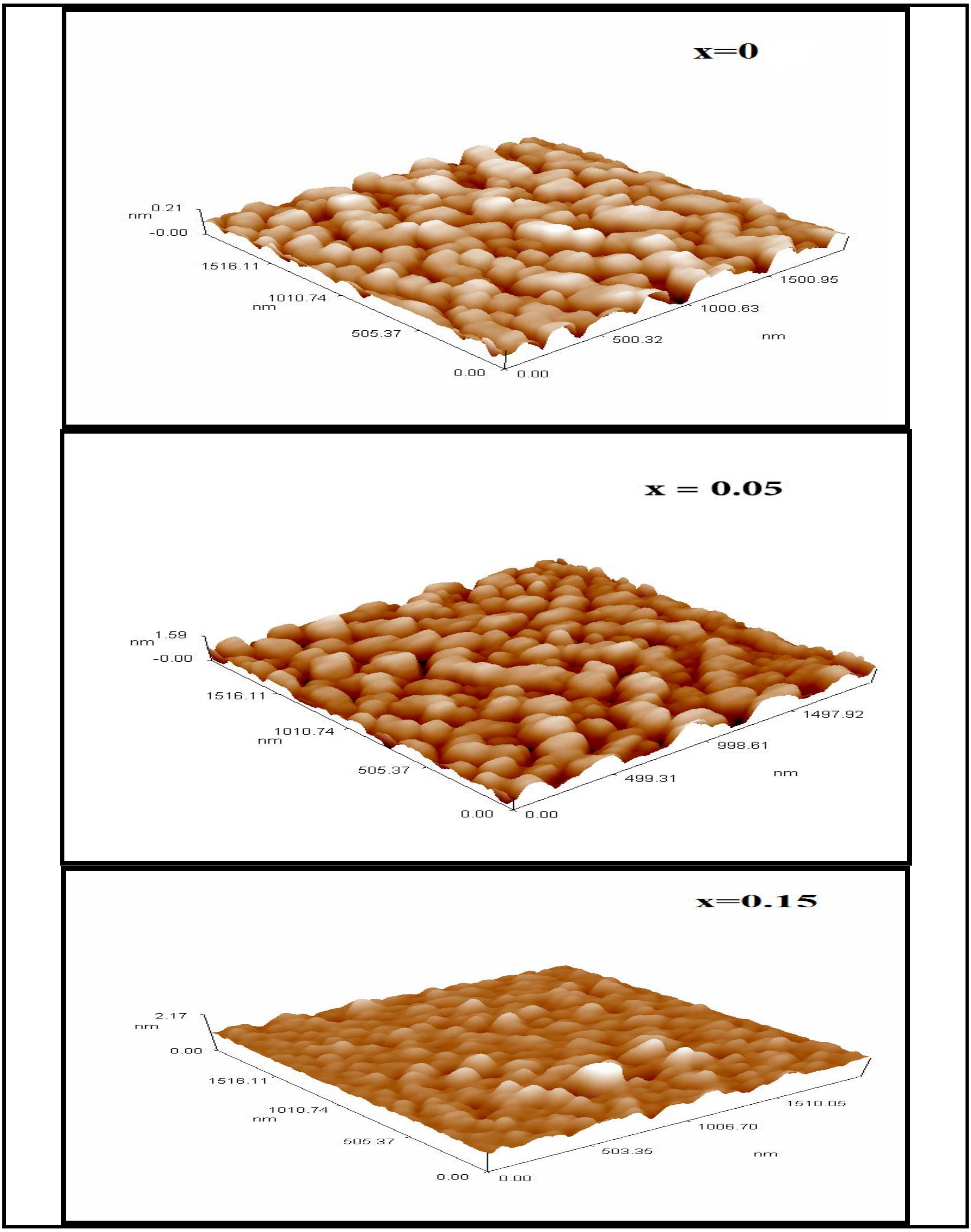

Fig. 2: AFM pictures for $(Sb_2S_3)_{1-x}Sn_x$ films 500 nm in thickness with different Sn contents (x=0, 0.05 and 0.15).

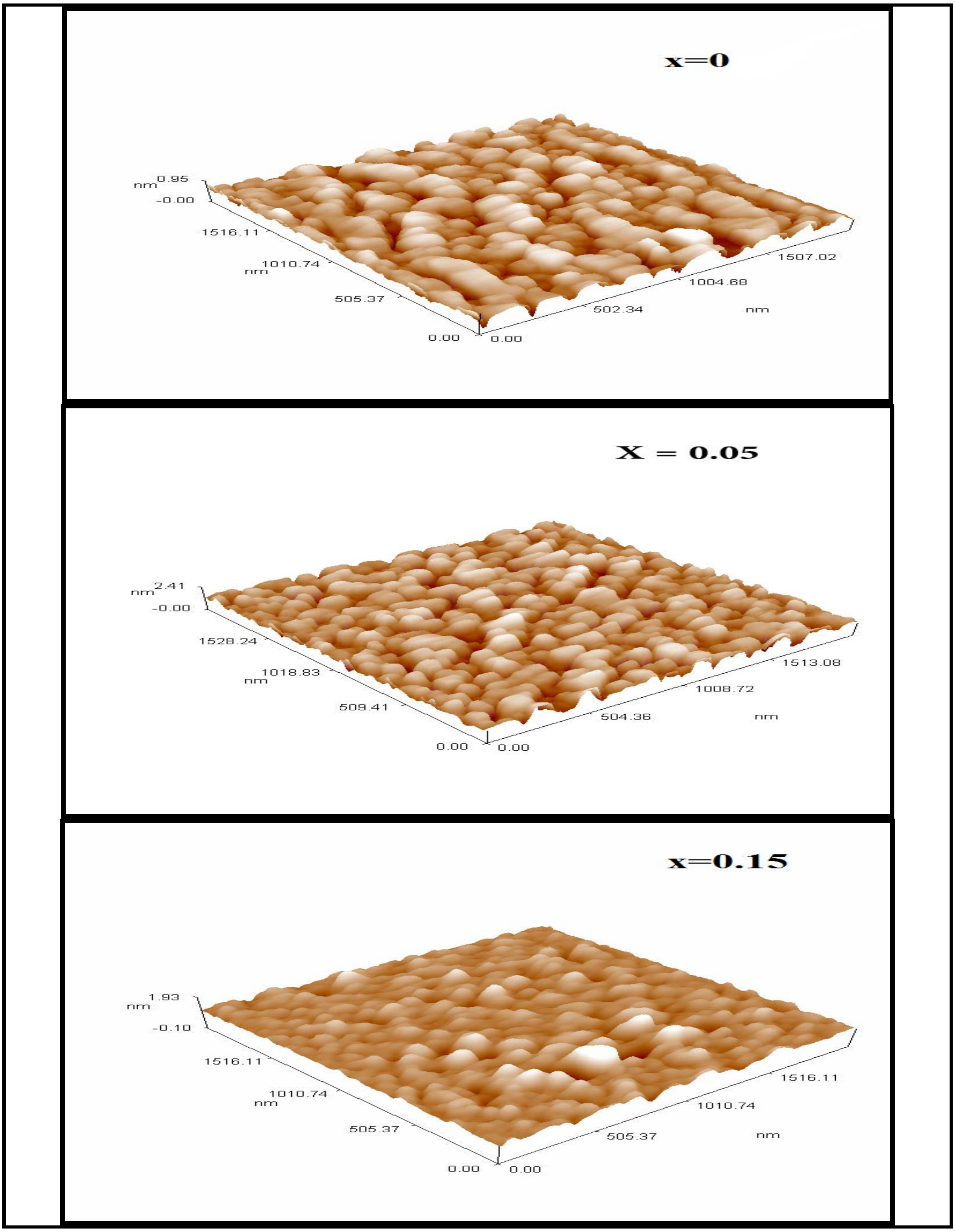

Fig. 3: AFM pictures for $(Sb_2S_3)_{1-x}Sn_x$ films 700 nm in thickness with different Sn contents (x=0, 0.05 and 0.15).

Table1: Average grain size and average roughness for $(Sb_2S_3)_{1-x}Sn_x$ 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 $(Sb_2S_3)_{1-x}$ 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

$$\sigma = \sigma_o \exp(-\frac{E_a}{k_B T}) \qquad (2)$$

where σ is conductivity at temperature T, σ_0 is constant, k_B is the Boltzmann constant and Ea is the activation energy. It is clear from these figures that there are three activation energy and hence three transport mechanism for $(Sb_2S_3)_{1-x}Sn_x$ 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: Ea_1 is the activation energy required to transport electron from Fermi level to the extended states above the conduction band edge Ec, Ea_2 is the activation energy required to transport electron from Fermi level to the localized below the conduction band edge, and Ea_3 is the activation energy required to transport electron between localized states at Fermi level.

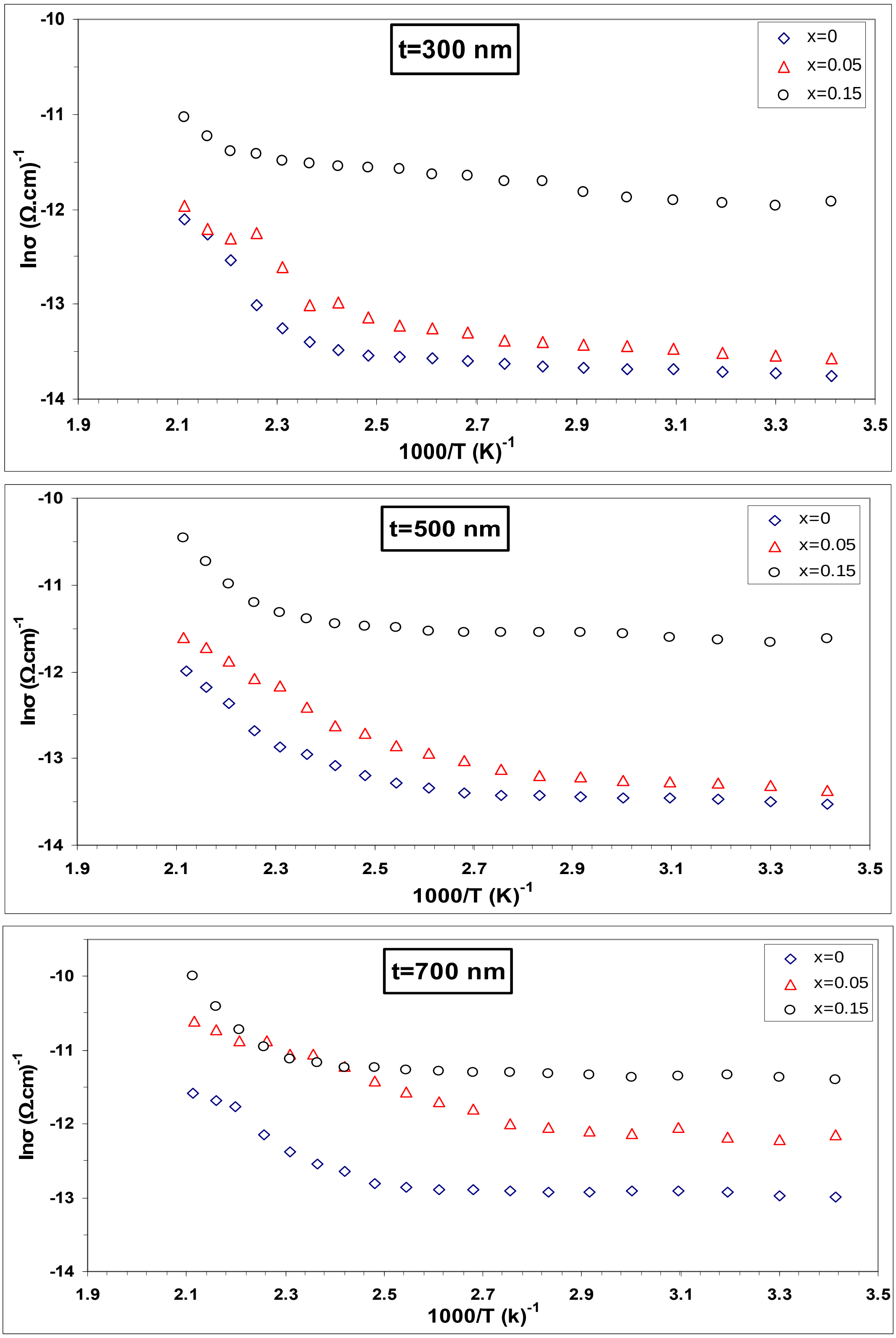

Fig. 4: The relation between Ln(σ) versus reciprocal of temperature for ($Sb_2S_3)_{1-x}Sn_x$ films with different Sn content and thicknesses.

The increasing of thickness has no effect of the number on transport mechanisms of the system $(Sb_2S_3)_{1-x}Sn_x$. The variation of Ea for as -deposited $(Sb_2S_3)_{1-x}$ 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 0.3292eV when the thickness increases from 300nm to 700nm 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_2S_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.

Table 2: The values of E_{a1}, E_{a2} and E_{a3} and the temperature ranges for $(Sb_2S_3)_{1-x}Sn_x$ films with different Sn content and different thickness.

t (nm)	X	Ea$_3$ (eV)	Temp.Range (K)	Ea$_2$ (eV)	Temp. Range (K)	Ea$_1$ (eV)	Temp.Range (K)	σ $_{RT}$*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 (μ_H) for $(Sb_2S_3)_{1-x}Sn_x$ 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, while for high thicknesses (t =500 and 700)nm with tin content (x=0, 0.05 and 0.15) the prepared samples reveal positive Hall coefficient (p–type charge carriers), i.e. Hall voltage increases with the increase of the current. It is well established fact that $(Sb_2S_3)_{1-x}$ 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 $(Sb_2S_3)_{1-x}Sn_x$ film with different thicknesses and Sn content.

t (nm)	x	R_H (cm^3/C)*10^7	n_H (cm^{-3})*10^{11}	type	μ_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 $(Sb_2S_3)_{1-x}Sn_x$ for low thickness and tin content. Increase of thickness improved the structure of the prepared thin films.

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