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Electrical properties of β -In₂S₃ thin films

A A El Shazly[†], D Abd Elhady^{†‡}, H S Metwally[†] and M A M Seyam[†]

[†] Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt

[‡] Faculty of Engineering, Ain Shams University, Abbasia, Cairo, Egypt

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Abstract. Stoichiometric thin films of In₂S₃ were prepared by the thermal evaporation technique; the as-deposited films were non-crystalline and the crystallinity was built in on annealing at 423 K. The crystal structure as determined by both x-ray and electron diffraction showed that tetragonal films of β -In₂S₃ phase were obtained. Both dark electrical resistivity ρ and thermoelectric power (Seebeck coefficient S) were measured for films before and after annealing. The In₂S₃ films showed n-type conduction; the existence of two distinct activation energies ΔE_1 and ΔE_2 belongs to two types of level: a shallow level of $\Delta E_1 = 0.319$ eV before annealing and $\Delta E_1 = 0.166$ eV after annealing and deep levels of $\Delta E_2 = 0.61$ eV for as deposited films and $\Delta E_2 = 0.515$ eV for annealed film. The deep level was also detected by the space charge limited current technique and the trap density N_t is found to be $3.92 \times 10^{22} \text{ m}^{-3}$. The obtained results are explained on the basis of an energy diagram of β -In₂S₃ proposed by Garlick.

1. Introduction

In₂S₃ which belongs to the group of $A_2^{III}B_3^{IV}$ compounds is a reddish material stable in air [1]. It is a wide band gap semiconductor with high photoconductive and luminescent properties [2–4]. These desirable properties make this compound a promising optoelectronic material [5, 6]. In optoelectronic materials, third transition metal properties have aroused a great deal of interest [7, 8]. The transition metal impurities have been known to introduce deep levels in band gaps of semiconductors. These levels not only control number, and type of mobility carriers but also act as activators or killers in luminescent materials.

β -In₂S₃ thin films have been prepared by different techniques: reactively evaporating In in an atmosphere of sulphur [2], spray pyrolysis onto glass slides maintained at 623 K [9], chalcogenization of indium metallic electroplated layers in H₂S gas atmosphere at temperatures of 623 K to 673 K [10], and the slurry painting method from powder of the respective semiconductor followed by annealing in nitrogen and hydrogen [11].

The β -In₂S₃ crystals grown by chemical transport reaction at room temperature were found to behave as n-type semiconductors [6]. Thin films also showed n-type conduction and negative thermopower coefficient $S = -100 \mu\text{V K}^{-1}$ [12]. However, little interest has been paid to In₂S₃ prepared by thermal evaporation, so we find it worthwhile to study the electrical transport properties of the In₂S₃ thermally evaporated thin film form to throw some light on the deep levels existing within its energy gap.

2. Experimental procedure

Thin films of different thickness of In₂S₃ were prepared by the conventional thermal evaporation technique using a high vacuum coating unit (Edwards type E306 A). Optically

flat ($\sim 0.1 \lambda$) glass substrates of rectangular shape were used. The substrates were fixed onto a rotatable holder (up to 240 r.p.m.) to obtain homogeneous deposited films at a distance of 25 mm above the evaporator. When the vacuum chamber is pumped to 10^{-5} Torr, the material (Aldrich 99.999%) is allowed to evaporate. At the first stage of evaporation a shutter is used, and this is removed to allow the vapour to be deposited onto substrate with deposition rate equals to 4 nm s^{-1} at about 300 K during the deposition process. The film thickness and the rate of deposition are controlled using a quartz thickness monitor (model FTM4 Edwards). In order to prevent the oxidation of the samples, they were left inside the vacuum chamber until their temperature reached room temperature, then air was admitted to the chamber and the samples were taken out.

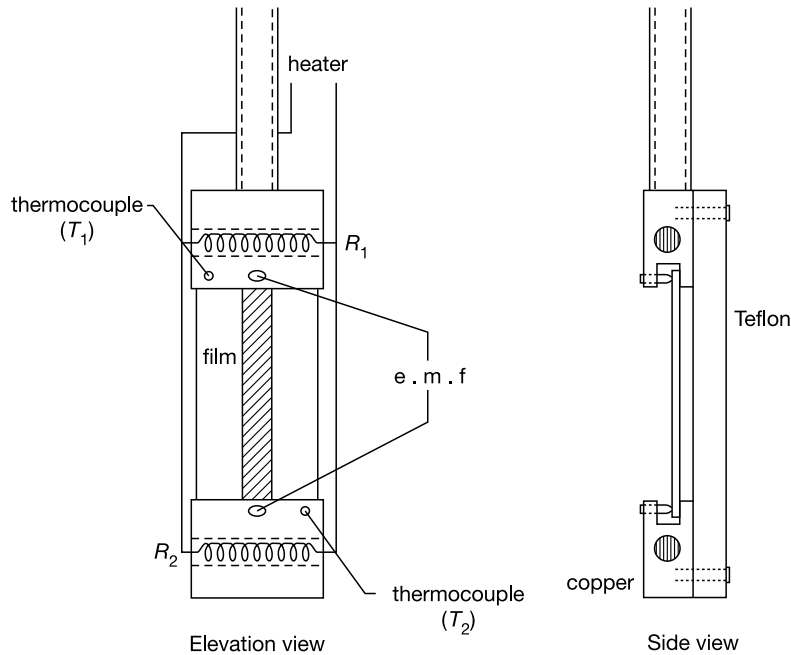


Figure 1. Holder used for the thermoelectric power measurement.

To study the effect of annealing temperature, the samples were annealed in vacuum for one hour at 423 K. The chemical composition of the obtained films is checked by energy dispersion x-ray spectroscopy (EDS) using a scanning electron microscope (JEOL 5400). Fully quantitative analysis results were obtained from the spectra by processing the data through a ZAF correction program. An x-ray diffractograph (Philips PW 10100), using Cu radiation operating at 40 kV and 25 mA, was used to investigate the crystal structure.

The electrical resistivities of In_2S_3 thin films of different thickness were measured in vacuum of 10^{-5} Torr in the temperature range of 300 K to 503 K using the two probe method. The ohmic contacts were made by evaporating high purity aluminum, through a suitable mask, onto the films. The ohmic nature of the contacts was confirmed by the linear I - V characteristic through above mentioned temperature range. The resistance of the films was measured using an electrometer (Keithley 617).

The thermoelectric power was measured using the differential technique, based on the following equation [13]

$$d\Delta E/dT|_{T_2} = S_{1,2}(T_2) = S_2(T_2) - S_1(T_2) \quad (1)$$

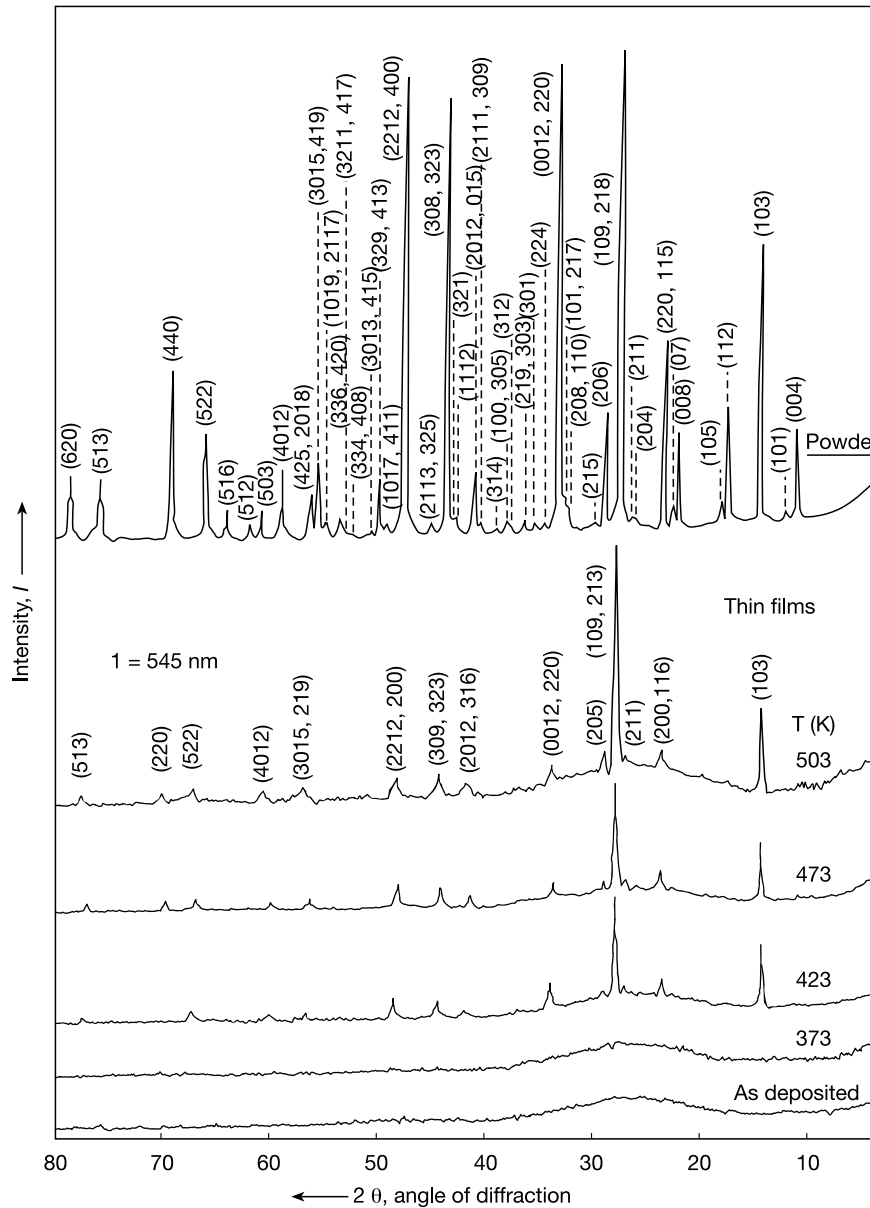


Figure 2. X-ray diffraction patterns of In_2S_3 thin films of thickness 545 nm with different annealing temperature in vacuum for one hour, with that of the as deposited compared to the powder form.

where $S_{1,2}(T_2)$ is the relative thermoelectric power between the materials 1 and 2 at the temperature T_2 , $S_1(T_2)$ and $S_2(T_2)$ are the thermoelectric power between film and contact material at T_2 . A special holder as shown in figure 1 was used. The temperatures T_1 and T_2 of the two ends were increased by using two different high power resistances R_1 and R_2 as a heat source and heat sink across the thin film under test. The sample has a T shape ($6 \times 0.5 \text{ cm}^2$). Before deposition of In_2S_3 thin film, a thick copper layer was

Table 1. Electron microscope analysis for In_2S_3 thin films of thickness 50 nm annealed at 423 K in vacuum for one hour, together with x-ray analysis.

From electron microscope		From x-ray analysis		
423 K		Powder	Card	
r (cm)	d (Å)	d (Å)	d (Å)	hkl
0.350	6.214	6.213	6.210	103
		4.929	4.927	105
		3.945	3.947	107
		3.810	3.811	200, 113
0.678	3.230	3.248	3.249	109, 213
0.838	2.631	2.691	2.694	0012, 220
1.072	2.080	2.067	2.074	309, 323
1.175	1.911	1.901	1.905	2212, 400

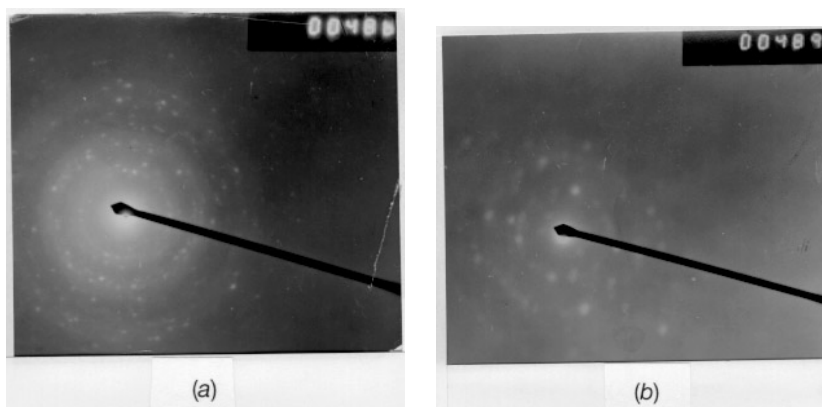


Figure 3. The electron microscope patterns of In_2S_3 films of thickness 50 nm (a) as deposited and (b) annealed at 423 K in vacuum for one hour.

deposited over the glass substrate to be used as electrode; afterwards the In_2S_3 film was thermally deposited. The temperature was measured by using a chromel–alumel thermocouple monitored by a microvoltmeter.

The electromotive force associated with the temperature gradient along the film was measured using an electrometer (Keithley 617) through copper leads pressed over the thin copper film. Since the thermoelectric power of the semiconductor is about 10^3 times that of metals [14], then the measured relative thermoelectric power between In_2S_3 thin films and copper is taken as the absolute value of the thermoelectric power (Seebeck coefficient S) of the In_2S_3 film.

3. Results and discussion

X-ray diffractograms obtained for In_2S_3 film (545 nm thick) either as deposited or after being annealed are shown in figure 2. As shown, the as-deposited sample has amorphous nature while those annealed in vacuum for one hour at 423 K have a polycrystalline nature of a tetragonal structure corresponding to $\beta\text{-In}_2\text{S}_3$ phase. The degree of crystallinity as well as the grain size of the individual crystallites were also found to increase with increasing

either the sample thickness or the annealing temperature. The Miller indices are given in the figure.

Figure 3 illustrates two electron diffraction patterns for In_2S_3 thin films (50 nm thick) as deposited and after being annealed in vacuum for one hour at 423 K respectively.

The analysis of these electron diffractograms showed that In_2S_3 has a polycrystalline nature of tetragonal phase belonging to β - In_2S_3 . However, the spotty patterns observed in the electron diffractograms may be attributed to the heating effect of the electron beam which changes the In_2S_3 films from amorphous to polycrystalline nature or even single crystal nature. The calculated d -spacing of the (hkl) lines observed from the x-ray technique and the electron diffraction pattern (table 1) showed that the annealed films of In_2S_3 are β - In_2S_3 phase.

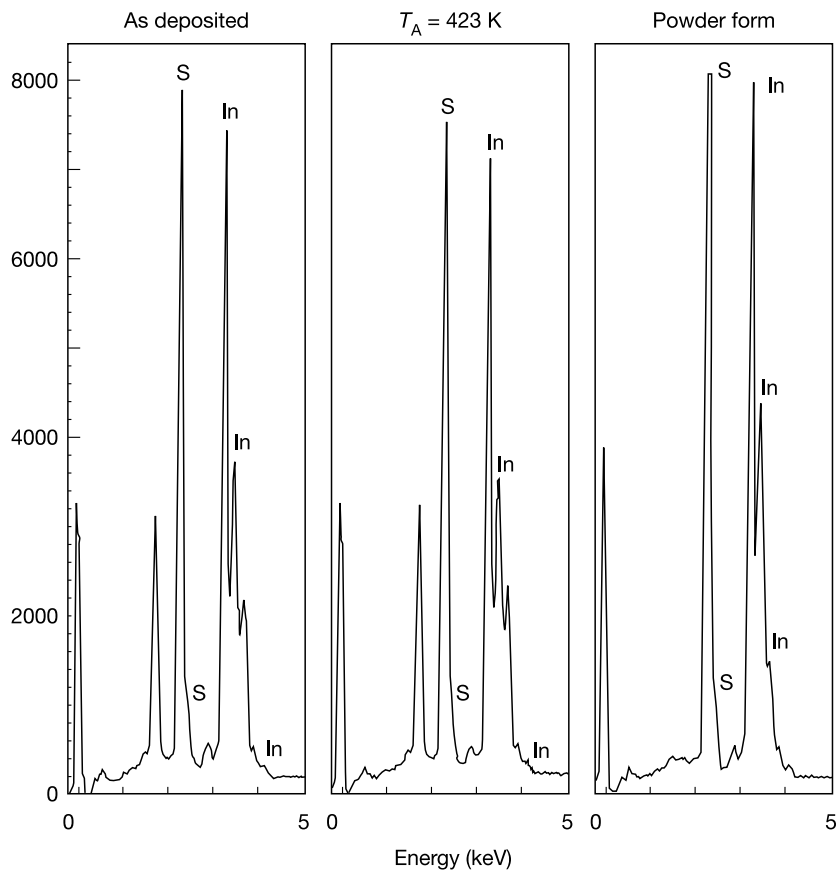


Figure 4. The energy dispersive x-ray spectrum of In and S elements for the as deposited and annealed In_2S_3 thin films compared to the powder form.

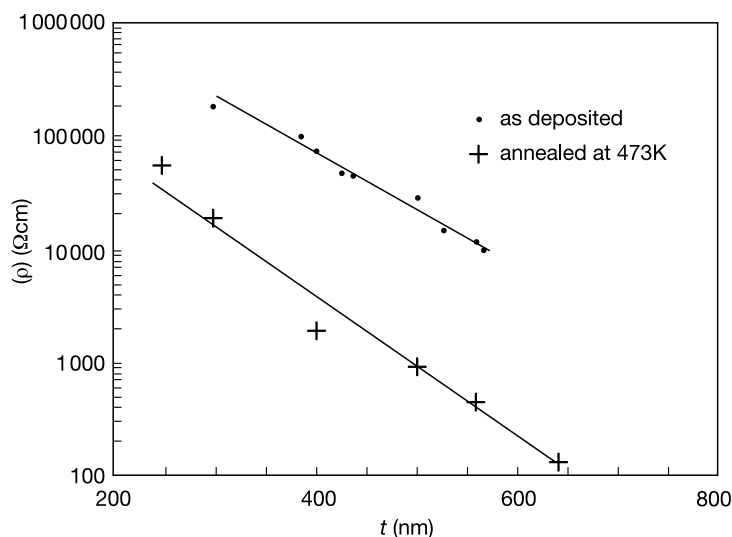
The energy dispersive analysis of β - In_2S_3 film before and after annealing shows that the obtained film is homogeneous; the stoichiometry and the composition of the film did not change after annealing as indicated by figure 4 and table 2. The first peak in the case of In_2S_3 films may be attributed to the effect of the substrate. Therefore it is absent in the powder.

Table 2. Elemental analysis of In_2S_3 .

Element	at.%		
	Bulk	As-deposited films	Annealed films
S	59.77	58.195	58.07
In	40.23	41.805	41.93
Total	100	100	100

To investigate the dark electrical resistivity of $\beta\text{-In}_2\text{S}_3$ film, samples of different thickness were prepared onto glass substrate at a deposition rate of 4 nm s^{-1} ; the thickness varied from 250 nm to 640 nm. Figure 5 shows the dark electrical resistivity ρ , measured at room temperature, as a function of film thickness. As observed, the dark electrical resistivity decreases exponentially with increasing film thickness. This behaviour can be attributed to lattice defect such as vacancies, interstitials and dislocations which might be formed through the first stage of the film growth. These defects add an extra percentage to the resistivity. Accordingly, the corresponding resistivity decreases as the film thickness increases. The reduction of the dark electrical resistivity with increasing film thickness may be also attributed to the increase of the size of the individual crystallites. It is clear that the annealed film of a certain thickness has a resistivity much smaller than that of the as deposited film. The reduction of the film resistance after annealing may be due to the increase of the grain size and/or the change from amorphous to crystalline structure as indicated from the structural studies carried out by both x-ray and electron microscope diffraction techniques.

The dark electrical resistivity ρ of each sample of the above mentioned films of different thickness was measured as a function of the sample temperature in the temperature range

**Figure 5.** The variation of the dark electrical resistivity ρ with film thickness (t) for the annealed $\beta\text{-In}_2\text{S}_3$ thin film in comparison with the as deposited films.

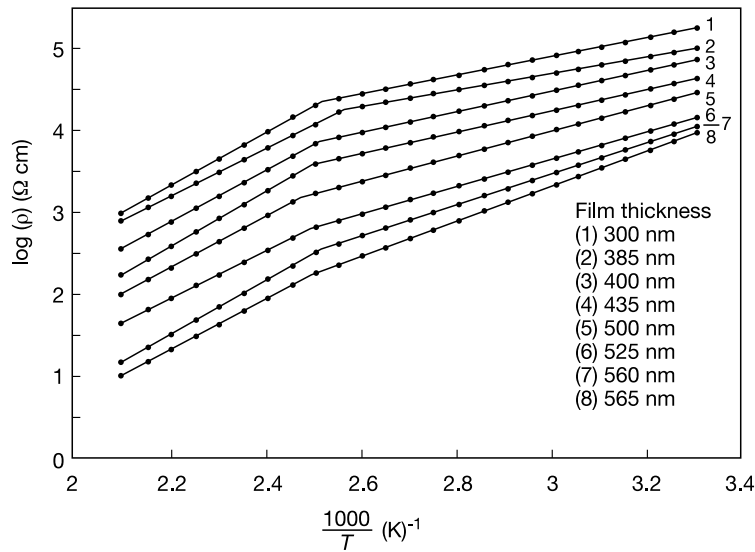


Figure 6. The dark electrical resistivity versus reciprocal temperature for as deposited In_2S_3 thin films of different thickness.

of 300–500 K. Figure 6 illustrates $\log \rho$ against $(1000/T)$ for as-deposited samples; each curve shows two distinct linear parts described by the well known equation

$$\rho = \rho_0 \exp(\Delta E/kT) \quad (2)$$

where ΔE is the thermal activation energy, k is the Boltzmann constant and T is the sample temperature. So the two distinct linear parts give two activation energies ΔE_1 and ΔE_2 corresponding to the existence of two impurity levels. ΔE_1 is about 0.319 eV, while ΔE_2 is about 0.61 eV. These values can be explained with the help of the tentative energy band diagram for the β - In_2S_3 single crystal proposed by Garlick *et al* [15]. According to this model, as given in figure 7, the energy gap includes some deep levels. Some of them are occupied by electrons and others are voids before transition. The electrons trapped in levels A jump to the conduction band, as they are thermally excited. The energy required for this process lies between 0.29 eV and 0.35 eV which is in harmony with the measured value of ΔE_1 .

On the other hand, the electrons trapped in levels C, when thermally excited, jump to levels B. The energy required for this process lies between 0.61 eV and 0.7 eV which is in good agreement with the measured value of ΔE_2 . The conduction process in the temperature range below 400 K may due to electrons moving from level A to the conduction band. In the temperature range over 400 K, the electrons going to level B; level C have no share in the conduction process as they are transferred from localized states to localized states. However, these transitions are accompanied by the existence of some voids in level C. These voids will allow some electrons to jump from valence band to levels C to fill them. Accordingly, some holes will be generated in the valence band. So, the conduction mechanism in the temperature range over 400 K was thought to be due to both types of charge carrier.

Figure 8 illustrates the relation between dark electrical resistivity and the reciprocal of temperature for β - In_2S_3 thin films of different thickness annealed in vacuum for one hour at 473 K. The values of the activation energies are $\Delta E_1 = 0.166$ eV and $\Delta E_2 = 0.515$ eV. The decrease in ΔE_1 for the shallow levels as a result of annealing indicates that these

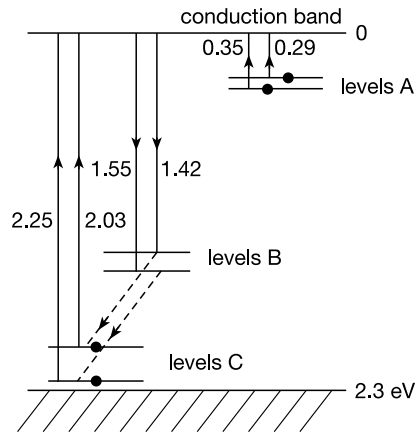


Figure 7. Tentative energy band diagram for β - In_2S_3 . States void of electrons before transition. States void of electrons before transition.

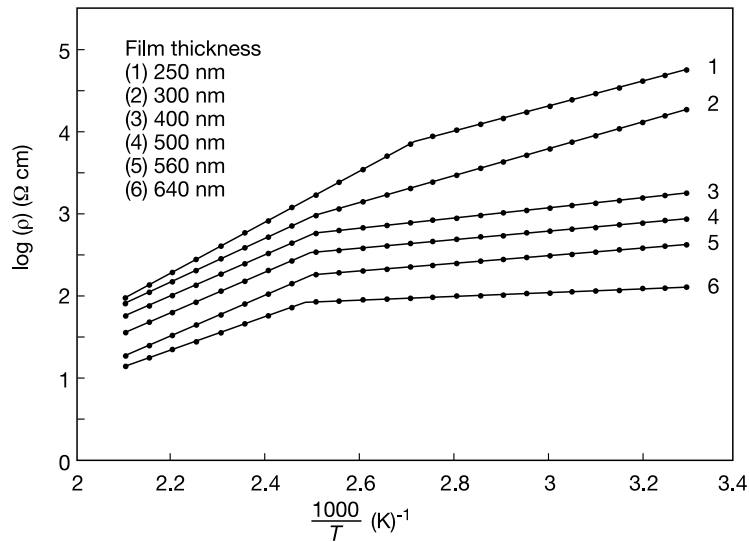


Figure 8. The dark electrical resistivity versus the reciprocal temperature for annealed β - In_2S_3 thin films of different thickness.

levels are structure defects levels. The deep level C is not affected by annealing.

Figure 9 represents the variation of thermoelectric power (Seebeck coefficient S) for the as-deposited In_2S_3 films of different thickness with temperature. The different curves exhibited close similarity in their general behaviour: all samples have a negative Seebeck coefficient indicating that In_2S_3 films behave as n-type semiconductors. The thermoelectric power (Seebeck coefficient) increases gradually at first with increasing the temperature until it reaches a maximum value, then it decreases gradually with increasing temperature. So, the figure can be divided into two regions, I and II: the first region exists below 400 K, which is in harmony with the behaviour of ρ as a function of $1000/T$. In the first region, the thermoelectric power is due to the free electrons generated from the shallow levels while the decrease of the thermoelectric power in the second region is due to the ionization of the

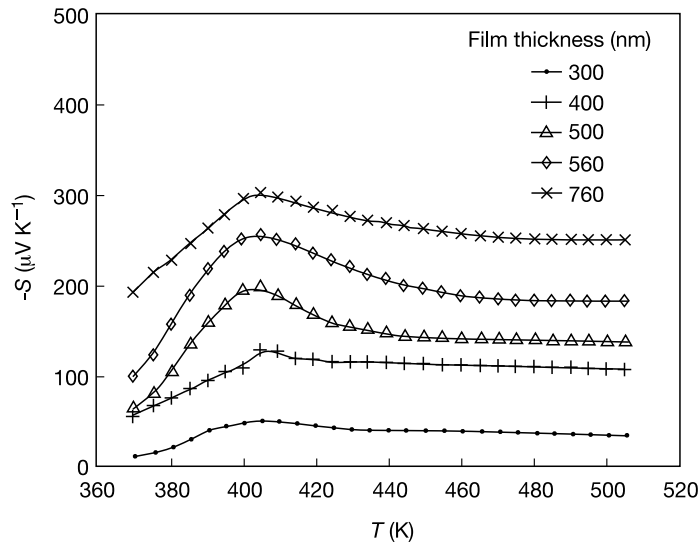


Figure 9. Thermoelectric power (S) versus the temperature (T) for as deposited In_2S_3 thin films of different thickness.

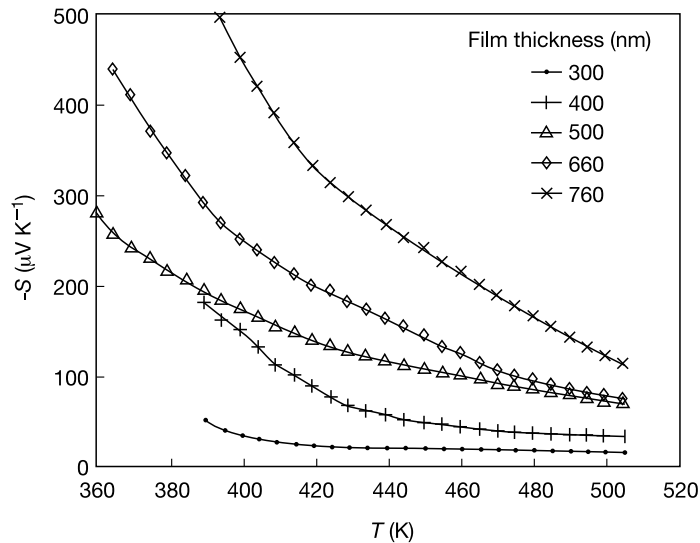


Figure 10. Thermoelectric power (S) versus the temperature (T) for annealed β - In_2S_3 thin films of different thickness.

deep level. These results are in agreement with that obtained for In_2S_3 films prepared by chemical deposition [11].

Figure 10 shows the variation of the Seebeck coefficient with temperature for β - In_2S_3 thin films of different thickness annealed at 473 K for one hour. The thermoelectric power of all films decreases with increasing the sample temperature, this is due to disappear of the shallow levels after annealing. The value of the thermoelectric power for the annealed sample is much smaller than that before annealing this may be due to holes generated from level C as mentioned before.

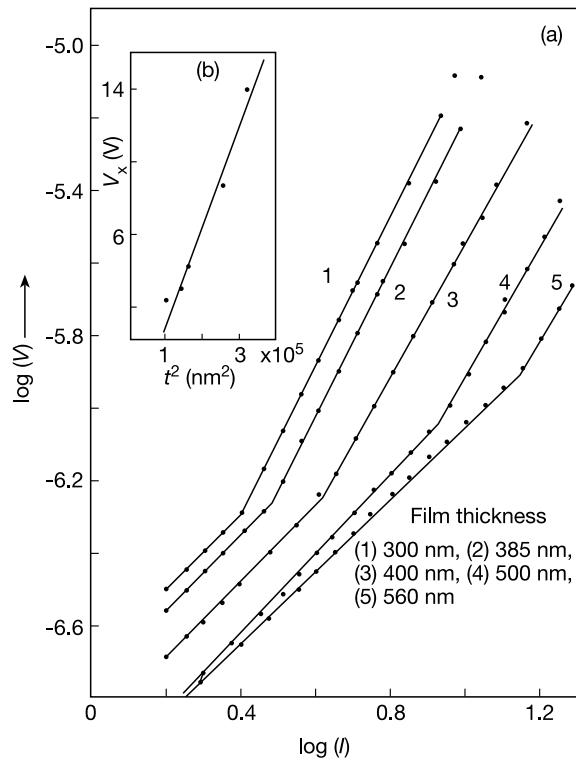


Figure 11. (a) I - V characteristics of In_2S_3 thin films of different thickness for as deposited In_2S_3 samples. (b) Dependence of V_x versus t^2 of In_2S_3 thin films for as deposited samples.

The I - V characteristics for In_2S_3 thin films in a sandwich configuration were measured for films of thickness from 300 nm to 560 nm. As shown in figure 11(a), at low voltage an ohmic region is obtained followed by a quadratic region ($I \propto V^2$). The cross-over voltage V_x was determined for all samples. Since the cross-over voltage is given by [16]

$$V_x = en_0 t^2 / \theta \epsilon \quad (3)$$

where e is the charge of the electron, n_0 is the free charge carrier concentration, t is the film thickness, $\theta (= n_0/n_t)$ is called the reduced factor or the ratio between the free charge carrier concentration n_0 and the trapped charge carrier concentration n_t , and ϵ is the dielectric constant. As expected, a graphical representation of V_x as a function of t^2 will yield a straight line shown in the top part of figure 11. The slope of this relation ($en_0/\theta\epsilon$) was found to be $5.45 \times 10^{13} \text{ V m}^{-2}$. According to Lampert theory, the quadratic region, the current density J is given by [16]

$$J = (9/8)\mu\theta\epsilon(V^2/t^3) \quad (4)$$

where V is the applied voltage and μ is the mobility of the free charge carriers.

When J is plotted as a function of (V^2/t^3) , it yields a straight line as shown in figure 12, the slope of which, $(9/8)\mu\theta\epsilon$, was found to be $3.79 \times 10^{-15} \text{ A m V}^{-2}$. From electrical resistivity and Seebeck coefficient measurements and knowing that $\epsilon = 13.5$ [15], the two slopes were used to determine θ , n_0 and n_t . It was found that $\theta = 3.11 \times 10^{-11}$, $n_0 = 1.22 \times 10^8 \text{ m}^{-3}$ and $n_t = 3.92 \times 10^{22} \text{ m}^{-3}$. However θ can be also expressed as

follows [16]

$$\theta = N_c/gn_t \exp(E_t/kT) \quad (5)$$

where $N_c (= 2(2\pi mkT/h^2)^{3/2})$ is the effective density of states in the conduction band, g is the degeneracy factor for the traps ($= 2$) [7], n_t is the charge carrier concentration, E_t is the energy of the trapping level, k is Boltzmann constant and T is the temperature in kelvin.

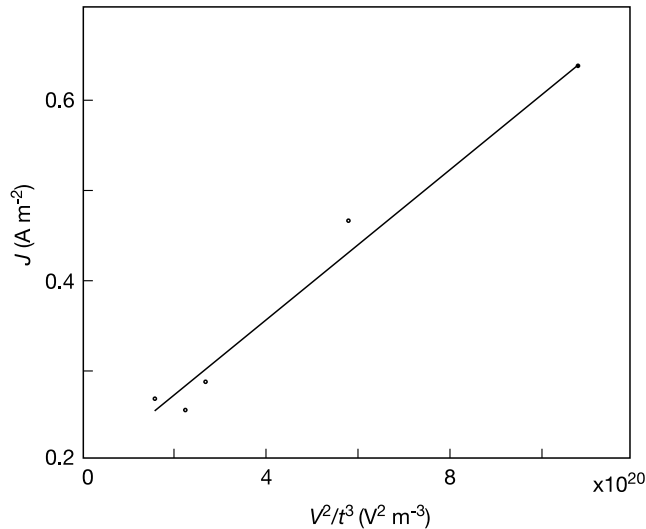


Figure 12. Dependence of the current density (J) on (V^2/t^3) for as-deposited In_2S_3 thin films.

It was found that E_t is about 0.62 eV in fair agreement with the mean value of ΔE_2 determined before through the dark electrical resistivity of In_2S_3 either as deposited (amorphous nature) or after being annealed (β - In_2S_3).

4. Conclusion

Stoichiometric films of In_2S_3 are prepared by the thermal evaporation for the first time. The as deposited films have amorphous nature while the pre-annealed films show polycrystalline nature with tetragonal β - In_2S_3 structure. The degree of crystallinity improves on annealing.

β - In_2S_3 films showed n-type conduction; the shallow levels are structure defects levels but the deep levels are characteristic of the material. The deep levels were detected by both resistivity and space charge limited current measurements.

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