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Defect characterization of spray pyrolised β-In$_2$S$_3$ thin film using Thermally Stimulated Current measurements

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Thermally Stimulated Conductivity (TSC) has been used to analyse defects in the novel material β-In$_2$S$_3$. These films were deposited using spray pyrolysis technique, varying In:*S* concentration ratio in the spraying solution. TSC measurements allowed the study of electrical property and non-radiative transitions, due to the defects present in the material. TSC spectra revealed four defects with their prominence varying with In:*S* concentration ratio. Samples with lower In concentration showed the presence and prominence of indium vacancy. A chemical impurity level due to the presence of chlorine was also detected. Even though sulphur vacancy existed in all the samples irrespective of the variation of In:*S* concentration ratio its effect decreased with the increase of sulphur concentration. Another defect level was also detected from TSC measurements at high temperature that was attributed to the replacement of sulphur by oxygen which was maximum in films prepared from a spray solution of In:*S* = 2:3 and minimum for 2:8. This high temperature defect level acts as a neutral center while all the other three levels were seen to be coulomb repulsive. Results from XPS analysis are found to be in good agreement with the TSC results.

1. Introduction

β-In$_2$S$_3$ polycrystalline thin films attract great attention nowadays because of their potential use in the fabrication of semiconductor devices. In the last few decades high efficiency solar cells were developed using cadmium sulphide as the window layer. But a cadmium free buffer layer [1] for heterojunction solar cells is better for environmental safety. This led to the development of a III–VI compound, indium sulphide that could replace cadmium sulphide in every way. In$_2$S$_3$ exists in three polymorphic forms α, β and γ [2]. β-In$_2$S$_3$, is a binary compound semiconductor having a defect spinel structure like that of γ-Al$_2$O$_3$ [3]. It belongs to the IIIA–VIA group of compounds with a stoichiometry $A_2^{III}B_3^{VI}$. Other existing compounds of this binary system are InS, In$_3$S$_4$, In$_4$S$_5$ and In$_6$S$_7$ [4]. III$_2$–VI$_3$ compounds crystallize in a lattice containing ordered vacancies in the III sublattice (vac), and could be designated as vac-III$_2$–VI$_3$.

Several authors reported preparation of β-In$_2$S$_3$ through different techniques like chemical bath deposition [5–7], physical vapour deposition [5], vacuum evaporation [8, 9], MOCVD [10], electrodeposition [11], atomic layer epitaxy [1] spray pyrolysis [12–15] etc. Conductivity, Raman and photoconductivity studies on single crystalline β-In$_2$S$_3$, prepared using different techniques have been reported [4, 16, 17]. Structural [13], optical [12, 15, 18] and acoustic [14] properties of spray pyrolysed β-In$_2$S$_3$ are also reported. However the defect characterization of β-In$_2$S$_3$ is not yet studied or reported to the best of our knowledge. In the present work Thermally Stimulated Conductivity (TSC) is used as a tool for defect characterization and the results are compared with the X-ray Photoelectron Spectroscopy (XPS) analysis.

Efficiency of a solar cell is mainly affected by the electrical property of the thin film used, which in turn depends on the presence of the defect levels in the band gap of the material. TSC technique was therefore used to analyse defects in β-In$_2$S$_3$ thin films prepared using spray pyrolysis. This forms a simple non-isothermal technique that permits survey of gap states and determination of the activation energy and capture cross section of each trap level. The samples were also subjected to X-ray Photoelectron Spectroscopy (XPS) studies for more details. We could relate the

TSC results with the XPS and the photo response of the samples.

2. Theoretical details

TSC forms one of the relaxation techniques to study defects in solids. It is a simple, non-isothermal technique used to determine defect levels in the band gap of semiconducting materials and a plot of current versus temperature is called the "TSC spectrum." Location of TSC peak on the temperature scale enable to determine the value of activation energy and the capture cross section of that defect level. A single peak corresponds to a single trap, indicating that the carriers are trapped at a single level, while a TSC curve with several maxima corresponds to a combination of traps or defects. Thermally stimulated current 'I', due to a single trap of depth E (activation energy), with negligible retrapping and monomolecular kinetics is given by [19, 20].

$$I = I_0 \exp\left[-\frac{E}{kT} - \frac{\upsilon}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{kT}\right) \mathrm{d}T\right] \quad (1)$$

where T_0 is the initial temperature, υ the attempt-to-escape frequency and β is the heating rate. The pre exponential factor I_0 is a weak function of temperature and I exhibit a maximum as a function of temperature.

Activation Energy is calculated using the equation,

$$E = 2kT_{\mathrm{m}}^2/(T_2 - T_1) \quad (2)$$

where $(T_2 - T_1)$ is the width of half maximum of the peak and T_{m} is the temperature of the peak maximum. Mott and Gruney [21] suggested a Capture cross section of

$$a = a_0\upsilon \quad (3)$$

from the TSC spectra, where $a_0 = 10^{-26}$ cm^2 s and $\upsilon = \beta(\alpha \exp \alpha)/T_{\mathrm{m}}$ and α is defined as $\alpha = E/kT_{\mathrm{m}}$.

3. Experimental details

3.1. Material preparation

β-In_2S_3 thin films were prepared using spray pyrolysis technique [22, 23] (Table I). Samples were prepared by varying In/S ratio in the solution by varying the molar concentration of indium chloride ($InCl_3$) and thio-urea ($CS(NH_2)_2$). In all the cases, rate of spraying of 400 ml solution was fixed to be 20 ml/min and substrate temperature was fixed at 300°C. The samples chosen for the study were varied in In:S concentration ratio from 2:1 to 2:8, keeping In concentration fixed at 2 in the spray solution. Two more samples were prepared having In:S ratio as 1.2:8 to 2.5:8, keeping S concentration fixed at 8 in the spray solution. All the samples were then coded as T_1 to T_6. All were yellow in colour with resistance of the order of Mega ohms. Band gap was estimated to be ≈2.6 eV from the absorption studies. Thicknesses of the films were measured using stylus technique and was found to be of the order of 1 μm. Hot probe measurements confirmed the n-type conductivity of these films.

TABLE I Samples of β-In_2S_3 prepared from varied indium to sulphur concentration ratio in the spraying solution

Sample code	In:S atomic concentration ratio in the spraying solution	Resistance of the samples
T_1	2.0:1	>2000 MΩ
T_2	2.0:3	10 MΩ
T_3	2.0:6	20 MΩ
T_4	2.0:8	50 MΩ
T_5	1.2:8	>2000 MΩ
T_6	2.5:8	30 MΩ

3.2. TSC experiment

For TSC measurements, samples were provided with electrodes using silver paste at a separation of 0.5 cm. Sample was loaded on the cold finger of a Liquid Nitrogen Dewar. Initially sample was cooled to 100 K (T_0) in a vacuum of 10^{-2} Torr and then it was optically excited for a constant duration of time 1 min using a white light of (power density 10 mW/cm^2). After this it was linearly heated keeping heating rate at 3 K/min. Current was measured along the film plane using Keithley Source Measure Unit SMU (K236) during the thermal scan from 100 to 500 K under a biasing of 30 V. TSC measurements were done on samples having different In:S stoichiometric ratios to confirm the defect levels. XPS spectra was recorded using ULVAC–PHI unit (Model: ESCA 5600CIM) employing argon ion sputtering (Voltage 3 kV, raster size 3 × 3 mm^2, pressure 10^{-6} Pa) and elemental analysis was done at an interval of 2 min, referred as cycle and the peak shift was corrected using carbon peak.

4. Results and discussion

4.1. Identification of the defects

TSC measurements carried out on different samples T_1 to T_6 (Table I) are presented in Fig. 1. These spectra revealed some peaks and shoulders which indicated that this material had a continuous distribution of defects rather than a single defect level in its band gap. Gaussian Fitting was done on the TSC curve using Microsoft Origin 0.6 to resolve the peaks and this led to the identification of traps with activation energies 0.1, 0.26, 0.43 and 0.82 eV. Their capture cross sections were of the order of $\approx 10^{-28}$, $\approx 10^{-26}$, $\approx 10^{-25}$ and $\approx 10^{-20}$ m^2 s respectively (Table II). Effect of these levels was found to vary with the variations of the preparation parameter and In:S ratio as it was clearly evident from the variation in the peak intensities of the TSC spectra. It was also observed that these traps existed only below 475 K, above which the sample showed high conductivity indicating the intrinsic conductivity of the material.

4.2. Effect of variation of In:S concentration ratio from 2:1 to 2:8, keeping In concentration fixed at 2 in the spray solution

TSC measurements taken on samples T_1 to T_4 of the Table I are as shown in Fig. 1. Measurement was carried

TABLE II Results analyzed from TSC measurements

Trap code	Activation energy (eV)	Temperature location from TSC curve (K)	Capture cross section (m^2 s)	Identified defect
I	0.10	160	$\approx 10^{-28}$	Indium vacancy
II	0.26	230	$\approx 10^{-26}$	Chlorine impurity level
III	0.43	320	$\approx 10^{-25}$	Sulphur vacancy
IV	0.82	450	$\approx 10^{-20}$	Replacement of sulphur by oxygen

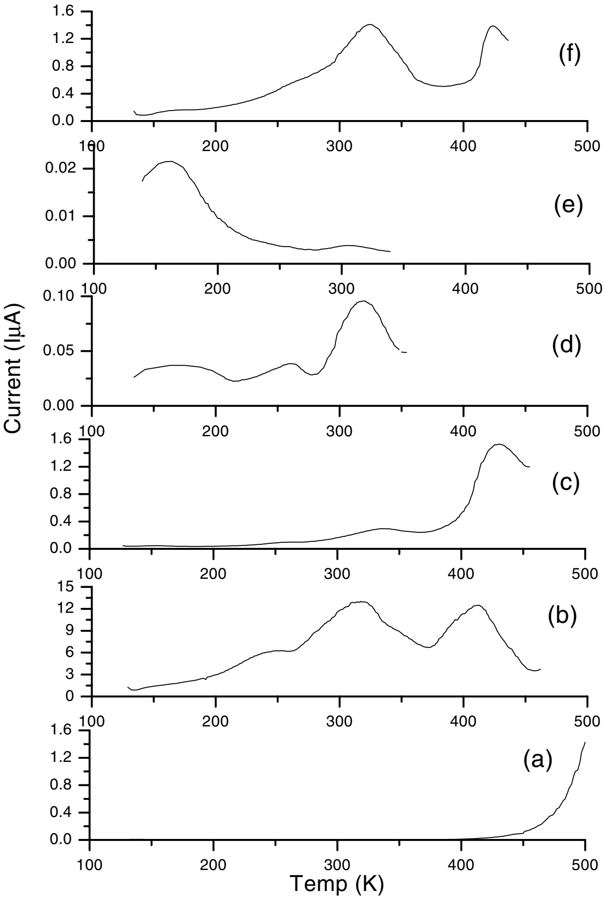

Figure 1 TSC spectra of β-In_2S_3: (a) In/$S = 2/1$, T_1; (b) In/$S = 2/3$, T_2; (c) In/$S = 2/6$, T_3; (d) In/$S = 2/8$, T_4; (e) In/$S = 1.2/8$, T_5; (f) In/$S = 2.5/8$, T_6.

out for optical excitation of 1 min and for a fixed heating rate of 3 K/min (0.05 K/sec). Variation of the TSC curve with the change in sulphur concentration ratio is clearly visible in this case. TSC curve of sample T_1 showed no peaks, since it was highly amorphous, as revealed through XRD studies (Fig. 2). From the other three TSC curves, four peaks could be detected with activation energies 0.1, 0.26, 0.43 and 0.82 eV. The 0.1 eV defect level was observed only for sample T_4 that was prepared from a spray solution of high sulphur concentration i.e., comparatively lower In concentration. It disappeared as the sulphur concentration in the spray solution decreased (sample T_2 and T_3, Fig. 1). Other defects of 0.26 eV and of 0.43 eV activation energies were observed in all the TSC spectra irrespective of the In:S ratio in the spray solution. But the peak intensity varied from sample to sample. The effect of the high temperature defect at 0.82 eV decreased with the increase of sulphur concentration in the spray solution. Its effect was most prominent in sample T_2, whose In:S concentration ratio in the spray solution was 2:3.

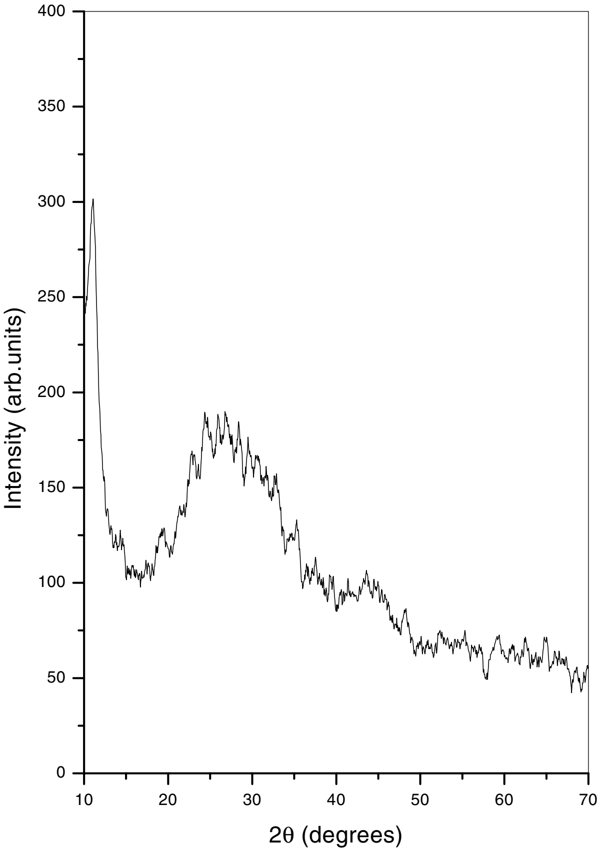

Figure 2 XRD analysis of β-In_2S_3, sample T_1.

4.3. Effect of variation of In:S concentration ratio from 1.2:8 to 2.5:8, keeping S concentration fixed at 8 in the spray solution

Variation of In in the In:S concentration ratio of the spray solution has a great influence on the electrical property of In_2S_3 thin film as observed from the TSC measurements. For the confirmation of the defects detected in β-In_2S_3 in the earlier section, TSC measurements were performed by varying the In:S concentration ratio of the spray solution for fixed sulphur concentration, $S = 8$. Here also rate of heating was 3 K/min and optical excitation was for 1 min. TSC spectra of sample T_4, T_5, and T_6 are also presented in Fig. 1. The spectra were similar to that of the TSC curves of earlier section. Activation energies corresponding to the TSC peaks observed at 160, 230, 320 and 450 K, was calculated as 0.1, 0.26, 0.43 and 0.82 eV and were similar to the results of the earlier section. But it was noted that for sample T_4 and T_5, 0.1 eV level is seen to be more prominent. Its effect was greatest for sample T_5 whose In:S ratio in spray solution was 1.2:8 [least indium and highest sulphur concentration]. Intensity of the peak corresponding to 0.1 eV level decreased in the sample prepared using spray solution of higher indium concentration (i.e., 2:8 and 2.5:8, T_4 and T_6). Actually this level vanished for sample T_6, as In:S ratio in the spray solution was 2.5:8. The 0.26 eV trap was present for T_4 and T_6 and disappeared for sample T_5, whose In:S ratio in the spray solution was 1.2:8. Though the 0.43 eV level was observed to be present in all the spectra its peak intensity decreased as In concentration decreased or when sulphur concentration increased. The high temperature peak corresponding to the activation energy 0.82 eV is observed only for sample T_6 whose In:S concentration ratio in spray solution was 2.5:8. Though this level appeared in the TSC curve of other samples it had only a negligible effect and could not be fitted properly for samples of lower In concentration, T_4 and T_5.

4.4. XPS analysis

The XPS spectra of a sample give the composition of the thin film. From the value of the binding energy obtained in XPS analysis of In_2S_3 (Fig. 3) it is clear that the film formed from different In:S concentration ratio in the spray solution are Indium Sulphide. From Fig. 3 presence of chlorine was observed throughout the film. Its percentage being least for sample T_5 whose In:$S = 1.2:8$ (in spray solution). Oxygen was present at the surface with a binding energy of 532.49 eV whose percentage was maximum for sample T_2, whose In:S concentration ratio was 2:3. Thus oxygen and chlorine present in the samples can act as major impurities in the spray pyrolised β-In_2S_3 thin films. Infact the XPS results were well agreeing with the TSC results.

4.5. Discussion

A comparative study of TSC on different samples of spray pyrolised β-In_2S_3 revealed four traps in the material. The intensity of the peak corresponding to 0.1 eV activation energy (160 K) increased with the decrease of In concentration. Its capture cross section was determined to be of order of 10^{-28} m^2 s. This defect was observed only in TSC studies of lower In concentration i.e., sample T_4 and T_5. From Fig. 1, it was observed clearly that its peak intensity is greatest for sample T_5 (In:$S = 1.2:8$ in spraysolution) and it vanishes for

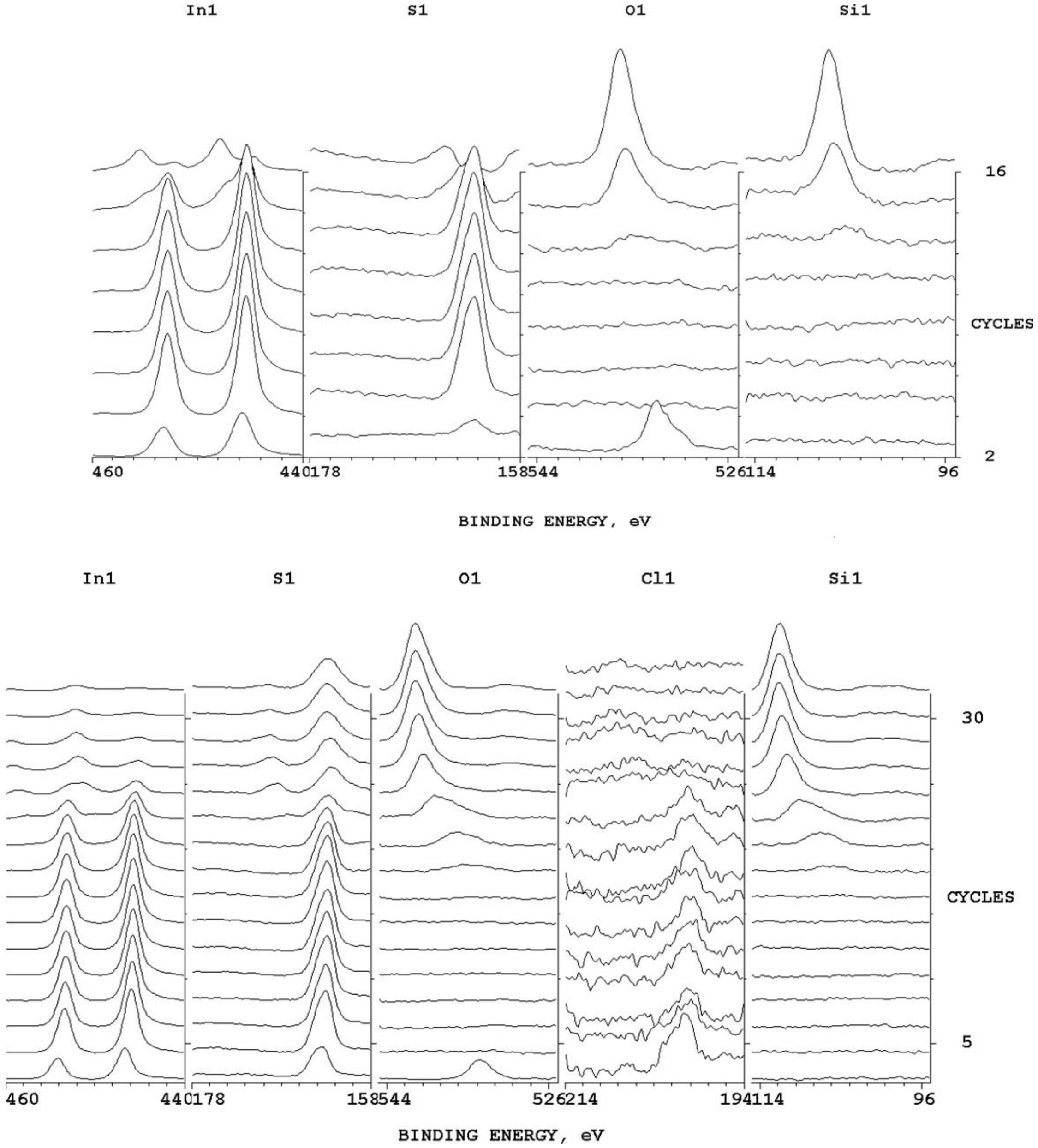

Figure 3 XPS analysis of samples T_2 and T_5.

sample T_6 whose In:S concentration ratio is 2.5:8 in spray solution. This indicates that 0.1 eV level may be a defect arising due to the indium vacancy. This level did not appear in sample T_2, T_3 and T_6, which might be due to the fact that, increase of concentration of In in the spray solution resulted in the filling of vacancy thereby vanishing the trap level at 0.1 eV.

The trap level of 0.26 eV around 230 K with a capture cross section 10^{-26} m^2 s existed in all the samples of indium sulphide except for sample T_5 (Fig. 1). As the percentage of In was least in this sample a high percentage of In vacancy existed in this sample. Presence of chlorine in the sample was revealed through XPS studies. While the XPS analysis showed only a small percentage of chlorine in sample T_5, chlorine was found to be present in higher percentages in all the other samples. Perhaps this defect at 0.26 eV is arising due to the chlorine impurity.

All the TSC spectra revealed another important peak, which arose just above the room temperature. Its activation energy was calculated to be 0.43 eV at 320 K, with a capture cross section of the order of 10^{-25} m^{2}s. This level was observed in all the TSC spectra with varying peak intensity depending on In:S concentration ratio in the spray solution. This revealed that this is a native defect whose prominence decreased when the sulphur concentration increased or indium concentration decreased in the stoichiometric ratio In:S of the spray solution. The peak intensity was observed to be highest for sample T_2 (whose In:S concentration ratio was 2:3) while it decreased for sample T_4 (whose In:S ratio was 2:8). Further with the decrease of In concentration for sample T_5 whose In:S ratio was 1.2:8, it was observed that this defect level had only negligible contribution to conductivity. This indicated that this defect decreased with increase of sulphur and hence may be a sulphur vacancy.

TSC measurements gave peaks only below 475 K, above which the current increases rapidly to several orders showing the intrinsic conductivity of β-In$_2$S$_3$. A high temperature peak was observed at 450 K, whose activation energy was calculated to be 0.82 eV. This defect had large capture cross section of the order of 10^{-20} m^2 s and effect of this level was observed to be most prominent for sample T_2 whose In:S concentration ratio is 2:3 in the spray solution. Sample T_2 showed low resistivity when compared to the other samples. Barreau *et al.* [24] reported that substitution of sulphur by oxygen induced high electrical conductivity and low resistivity in β-In$_2$S$_{3-3x}$O$_{3x}$ prepared using physical vapour deposition. Perhaps it is the replacement of sulphur by oxygen, which created such a deep impurity level in spray pyrolised β-In$_2$S$_3$ thin film. It was also observed that the effect of defect at 0.82 eV decreased with increase in sulphur. In the present work XPS studies show that the highest percentage of oxygen is in sample T_2.

In principle, any defect in the band gap has a finite cross section for capture of holes as well as electrons that is largely determined by the charge state of that trap. Defect state that is coulomb attractive to free electrons might act as neutral or repulsive to holes, showing a small capture cross section for hole when compared to electron. Thus capture cross section of a trap is a rough approximation, largely depending on its charged state, whether the trap is coulomb attractive, repulsive or neutral to the carriers of that material. In literature, values are reported comparing the range of the capture cross section with the coulomb potential [25]. In the present study capture cross-sections for the different defect levels are calculated and are tabulated in Table II. A general trend of increase of capture cross section with activation energy is observed. It is specified by Braunlich [25] that when the capture cross section is in the range 10^{-21} to 10^{-19} m^2 s the trap is neutral center, but when the range lies below 10^{-21} down to 10^{-26} m^2 s the trap acts as coulomb repulsive center and if the value was greater than 10^{-19} m^2 s then the center is coulomb attractive. From our observations and measurements we could conclude the defect level at 0.82 eV with a capture cross section $\approx 10^{-20}$ m^2 s is a neutral trap corresponding to the replacement of sulphur by oxygen. It is a ‘giant trap’, which is acting as a deep impurity and is responsible for most of the electrical property of β-In$_2$S$_3$. All the other traps being coulomb repulsive centers. Here we have taken capture cross section considering the particular temperature at which the peak occurs. But coulomb repulsive centers vary their capture cross section with temperature. Keating [26] has theoretically proved the temperature dependence of capture cross section affecting the thermally stimulated conductivity (emission of carriers).

Comparing all the TSC curves it could be concluded that least percentage of defects is present in sample T_5 whose In:S stoichiometric ratio in the spray solution was 1.2:8. Photo response measurements on this sample also revealed the same (Fig. 4).

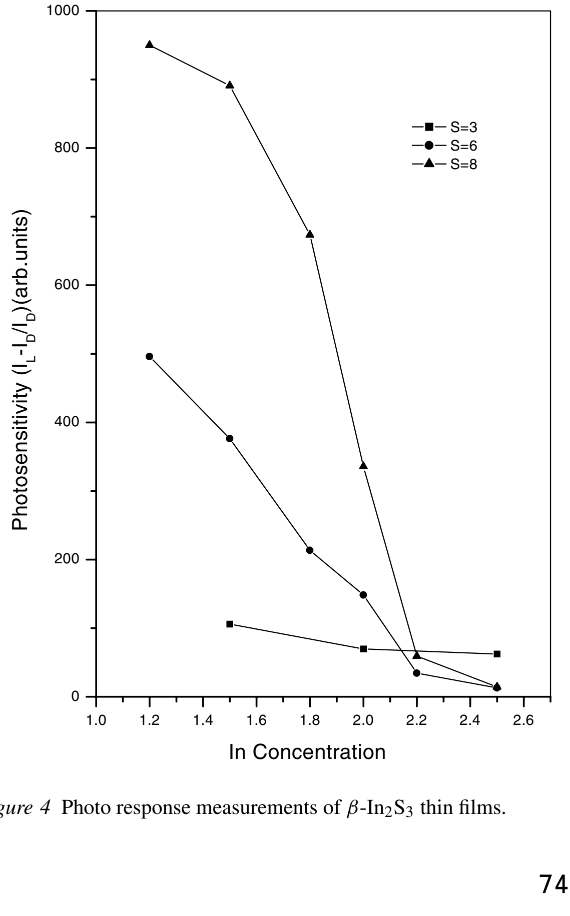

Figure 4 Photo response measurements of β-In$_2$S$_3$ thin films.

5. Conclusion

Defect characterization of the semiconducting thin films of β-In$_2$S$_3$ using Thermally Stimulated Conductivity studies revealed four trap levels with activation energies 0.1, 0.26, 0.43 and 0.82 eV in the band gap of this material. Variation of their prominence was observed for the different stoichiometric ratios of In:S. The results were verified using X-ray Photoelectron Spectroscopy (XPS) analysis. Samples with lower In concentration showed the presence and prominence of Indium Vacancy. Irrespective of the variation of In:S concentration ratio, chlorine impurity level and sulphur vacancy existed in all the samples. A high temperature defect level attributed to the replacement of sulphur by oxygen was also detected. Comparing the values of capture cross sections of these levels, we could conclude that three of these centers to be coulomb repulsive while the fourth to be a neutral center, which is mostly responsible for the electrical property of β-In$_2$S$_3$. XPS analyses on these samples are found to be in good agreement with the TSC results. Sample T_5 whose In:S ratio in the spray solution as 1.2:8 is found to have less defects and high photo response.

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