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Preparation and characterization of indium doped SnS thin films for solar cell applications

P. Thiruramanathan[1], G.S. Hikku[2], R. Krishna Sharma[*1], M. Siva Shakthi[3]

[1]Department of Physics, Mepco Schlenk Engineering College, Sivakasi-626005, India
[2]Centre for Nano Science and Technology, Mepco Schlenk Engineering College, Sivakasi-626005, India
[3]Centre for Research and Post Graduate Department of Physics, Ayya Nadar Janaki Ammal college, Sivakasi - 626 124, India.

Abstract: SnS compounds are potential candidates for the production of low cost solar conversion materials. They have recently attracted considerable attention because of their physical properties, which are suitable for optoelectronic device fabrication. Indium doped SnS thin films were fabricatedusing the spray pyrolysis technique and their structural,morphological and elemental analyses were analyzed by X-ray diffraction (XRD),scanning electron microscope (SEM) and energy dispersive analysis for X-ray (EDAX) respectively. The crystallite size of the pure SnS and indium doped SnS was calculated using the Debye Scherrer's formula. XRD result reveals that the crystallite size of thin films was reduced with increasein the dopant concentration. The EDAX results confirm the presence of indiumin the thin films and its atomic percentage increases as the doping concentration was increased.

Keywords: thin films, spray pyrolysis technique, doping, morphology, atomic percentage.

1 Introduction:

SnS is a p-type semiconductor compound and layered SnS is IV-VI compound crystallizing in the orthorhombic structure with an indirect band gap values ranges between 1.0eV and 1.5eV and direct band gap between 1.39eV and 2.33eV depending on the method of preparation and heat treatment temperature. Tin sulphide compounds in photo voltaic structures would decrease the production costs of solar cells, because the materials involved are cheap, non-strategic and abundant in nature(1-3).Tin sulphide has attracted attention because of their properties such as light absorbing material for photoconductors, photovoltaic conversion, holographic recording media, near infrared detector, etc. A large number reports has been published concerning SnS thin films as potential material for solar cells during the last decade (3).

Three forms ofSn-S compounds are found, which are interesting from the technical point of view. They are tin sulphide(SnS), tin di sulphide(SnS_2) and Sn_2S_3. $Sn_2S_3$is classified as a type I mixed valence compound with semiconductor behavior, whose optoelectronic properties are dependent on the crystalline structure and stoichiometry (4). The trends of current research in photo voltaic include preparation of non-toxic and earth abundant materials in thin films, dye sensitized solar cells and nanostructured materials. In thin film photo voltaic applications, cadmium telluride and copper indium gallium selenide are the leading materials used. These materials, both contain toxic and rare materials.Sulphide is less toxic than selenide, though efficiencies of sulfo-selenide device are up to 10.1% compared to that of sulphide devices which are only 6.8% efficient(5).Compare to the bath techniques, spray deposition offers a lesser quantity of material consumption. This is especially important for the environmental issues as well as efficient usage of rare materials. Spray pyrolysis technique used in this study, therefore it has been gaining attention, especially in energy storage, biomedical and photo voltaic applications. This method has been used to build thin films of wide band gap semiconductors on glass substrates. Various physical and chemical methods are used for the formation of SnS

thin films such as thermal evaporation, atomic layer deposition, electro deposition, chemical bath deposition and spray pyrolysis. Among them we have used spray pyrolysis technique for the formation of SnS thin films which is simple, versatile method and very efficient to produce the large area deposition and also can control the thickness of the film by the amount of spray solution. The variations in structure and morphology of the films with respect to deposition parameters are very essential to obtain good quality films for photovoltaic devices (6, 7).Generally, the surfaces of the thin films prepared by spray pyrolysis have rough morphology due to the difficulty in controlling the parameters of the spraying process and the size of the droplet. However, it remains as the useful technique for obtaining thin films for fundamental studies and for some specific applications (8). Doping of SnS thin films with In, Sb, Bi, Cu and Ag has been reported to improve their electrical and optical properties (9). Therefore, it is necessary to study doped SnSthin films for various applications(10). The recent investigations in the field of photo voltaics are directed towards the development of cost effective and nontoxic materials that can be easily synthesized by a simple and robust technology for solar cell fabrication. In this direction, attention has been focused on new materials, which are abundant in nature and can be easily processed to generate device grade material without posing any environmentalproblems (11). Fundamental research of pure phase SnS film growth is necessary to eventually discover to way improve solar cell efficiency. The SnS based solar cell is finding a method to grow pure phase SnS thin films without secondary phases such as Sn_2S_3, Sn_3S_4 and SnS_2 (12).Considering these facts spray pyrolysis technique was employed for the preparation of SnS thin films with tin chloride and thiourea as precursor. Also, their structural, morphological and elemental characterizations were carried out.

2 Materials and Methods:

2.1 Preparation of SnS thin film:

Indium doped SnSthin films were deposited on the glass substrateby a spray pyrolysis technique using tin chloride and thiourea as the precursor solution.$SnCl_4.H_2O$ and thiourea were dissolved separately in isopropyl alcohol and deionized water respectively, and were mixed with a fixed molar ratio of 1:3.The doping concentration of indium chloride varies as 0.0001M, 0.001M and 0.01M respectively. The substrate temperature,voltage in the dimmer and pressure in the oven was maintained at 300ºC, 230V and 1kg/cm^{2}respectively. Finally the spray rate of the solution was fixed at 3ml/min and the distance between the nozzle and the substrate was kept at 20cm. The as-prepared thin films show light gray in color, indicating the formation of tin mono sulphide compound.

$SnCl_4.5H_2O + NH_2CSNH_2 \rightarrow SnS$ + Gaseous Products	(1)

3 Results and discussion:

3.1 X-ray diffraction analysis:

The XRD pattern for the pure SnS and indium doped SnSthin films are shown in Figure 1. The XRD patterns were recorded in the range from 10º to 80º.Based on the results the structure of the thin films was transformed from orthorhombic to monoclinic with increasing the doping concentration.The XRD pattern of the pure SnS thin film shows only one reflection at 31.7º, which corresponds to the SnS phase. The films exhibited an orthorhombic structure with preferential orientation along (130) which was in goodagreement with the JCPDS No. 32-1361and it also shows that the deposited film has a polycrystalline nature and good crystalline structure because of its sharp structural peak(15). For 0.0001M, 0.001M and 0.01M indium doped SnS, the XRD peak was found at 31.69. This peak corresponds to the monoclinic structure of SnS with miller indices plane (430) obtained from JCPDS No. 47-1391.Aydin et.al. got the similar result for incorporation of silver in indium sulphide thin films by spray pyrolysis technique and the structure was transformed from cubic to mixed tetragonal/orthorhombic phase (16).

The XRD pattern shows that the amorphous natureof the thin film was enhanced by the doping level of indium in thin films. By increasing the dopant concentration, the thin filmshows shift in the 2θ and d-spacing values.With the addition of indium, the intensity of the peak was found to be reduced when compared to the pure SnS peak.The 0.01M indium doped SnS shows a very low intensity peak in the XRD spectrum recorded. This was because of the increased amorphous nature of the sample as the doping level of indium was increased.

The crystallite size of the film was calculated from the Debye-Scherrer formula,

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (2)$$

The crystallite size of pure, 0.0001, and 0.001M of indium doped SnS was 98nm, 42nm, and 11nm respectively. The crystallite size decreasing trend was observed with the increase in Indium doping concentration which was shown in Figure 2 where grain size was plotted against the concentration of the dopant.

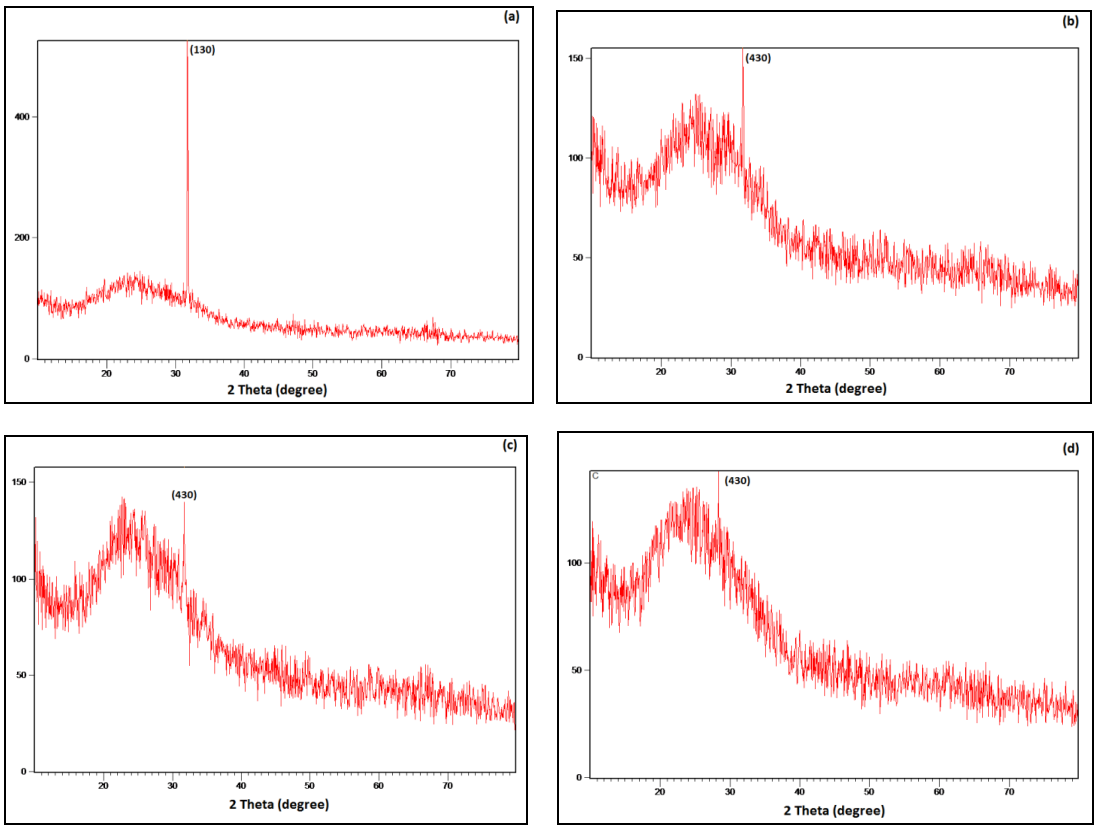

Figure 1 X-ray diffraction pattern of (a)undopedSnS thin film (b) 0.0001M Indium doped SnS thin film (c)0.001M Indium doped SnS thin film (d) 0.01M Indium doped SnS thin film

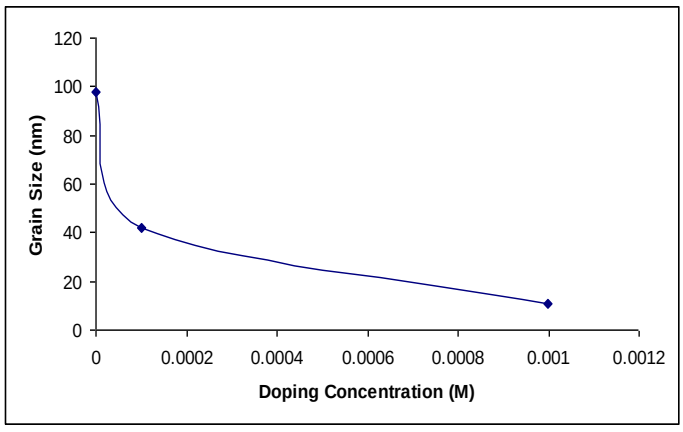

Figure 2 Variation of grain size with increase in doping concentration

As the concentration of dopant increases, the grain size was decreased. While considering the thickness of the film, it was first increased gradually and then decreased to a minimum value. The thickness of the film with various doping concentrations was tabulated in Table 1.

Table 1Thickness of thin film with respect to various doping concentration

Doping concentration (M)	Thickness of the film (µm)
0 (Un-doped)	0.73
0.0001	0.86
0.001	1.51
0.01	0.80

3.2 Scanning Electron Microscope analysis:

The reduction in particle size with respect to doping concentration was observed from SEM and is shown in Figure 3. The SEM image of the pure SnS thin films showsdistorted triangular shaped grains with an average particle size of 400nm (Figure 3 (a)). Altogether agglomerations are very less for the pure SnS thin film. 0.0001M indium doped SnS exhibits very small sized, but with similar shaped grains (Figure 3 (b)). As the concentration of indium is increased to 0.001M further reduction in size of the grains could be observed (Figure 3 (c)). The surface of the SnS thin film prepared with 0.01M indium doping shows no grain formation, but it exhibits almost sand like structure (Figure 3 (d)). Finally the effect of indium doping concentration reduces the grain size in the SnS thin films which was in accordance with the calculated crystallite size from the XRD peaks.

Uniform deposition of the SnS was observed from the surfaces of these thin films. The crystalline nature of these films was found to decrease as the indium concentration was increased. It was converted to amorphous with a complete sandy structure at a concentration of 0.01M of indium and above. Such a surface formation of thin films with indium doping increases the resistivity tremendously. The triangular shaped grains completely disappeared when increasing the molar concentration of dopant. These results were also in good agreement with the XRD result.

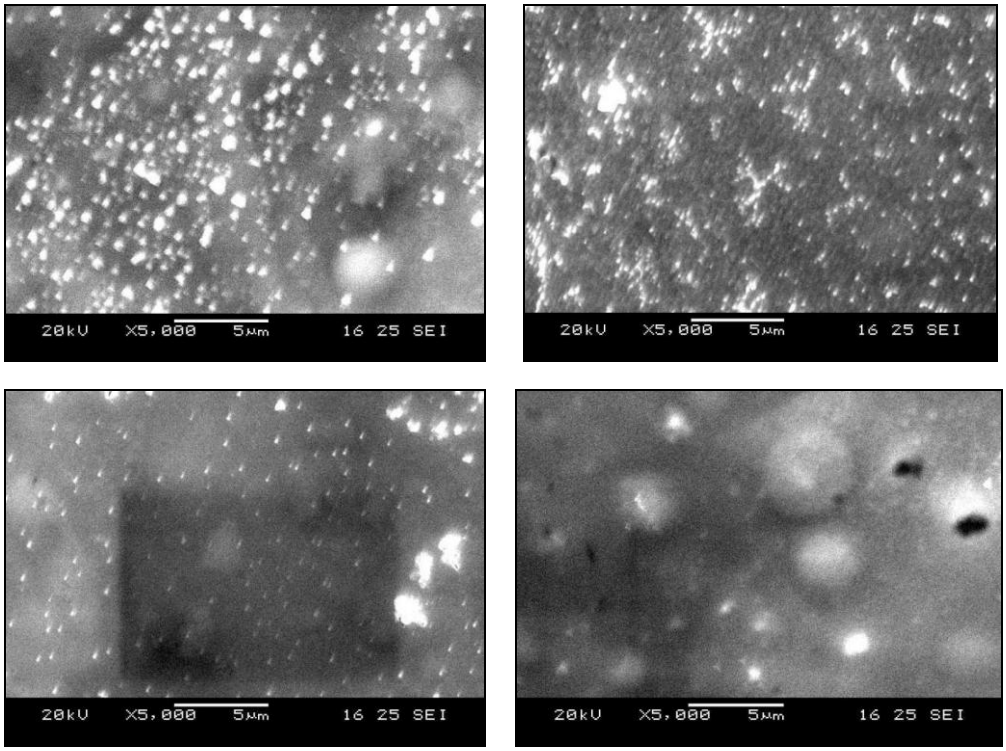

Figure 3SEM image of (a)undopedSnS thin film (b)0.0001M Indium doped SnS thin film (c)0.001M Indium doped SnS thin film (d)0.01M Indium doped SnS thin film

3.3 EDAX:

The EDAX spectrum of the pure SnS thin film showed the presence of tin and sulphur, but not indium(Figure 4 (a)). The atomic ratio of tin and sulphur in this sample was predicted as 74.95:24.05. The EDAX spectrum of sample in which indium was doped with the precursor concentration of 0.0001M is shown in Figure 4 (b), which exhibits the presence of indium. Similarly the EDAX spectrum corresponding to samples doped with indium with precursor concentration of 0.001M and 0.01M are shown in Figure 4 (c) and (d) respectively. They also revealed the existence of indium. The peaks corresponding to the binding energy of indium are found to occur correspondingly at 3.38KeV and 3.85KeV respectively.It predicted the presence of indium in the doped thin films and its atomic percentage increased as the doping precursor concentration increased. All the films showed the presence of tin and sulphur in the respective atomic percentage.

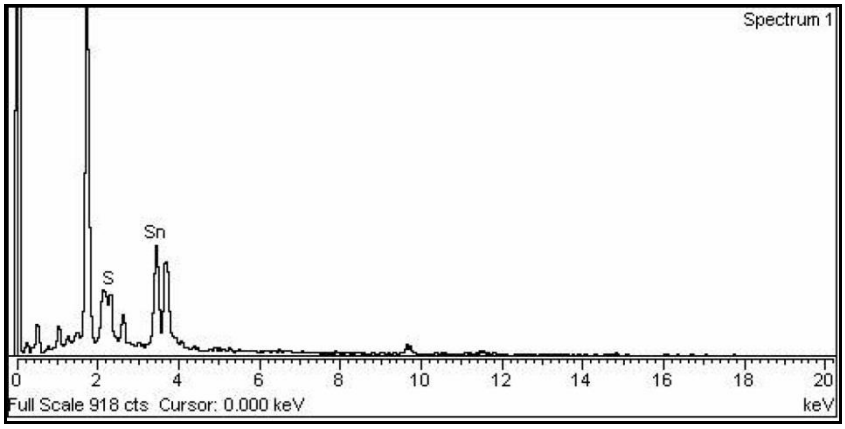

Figure 4 (a)EDAX spectrum of pure SnS thin film

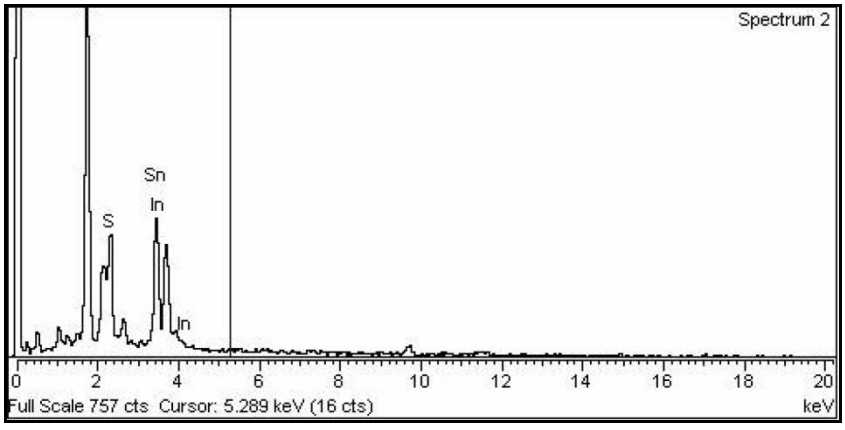

Figure 4 (b)EDAX spectrum of Indium doped SnS thin film at a concentration of 0.0001M

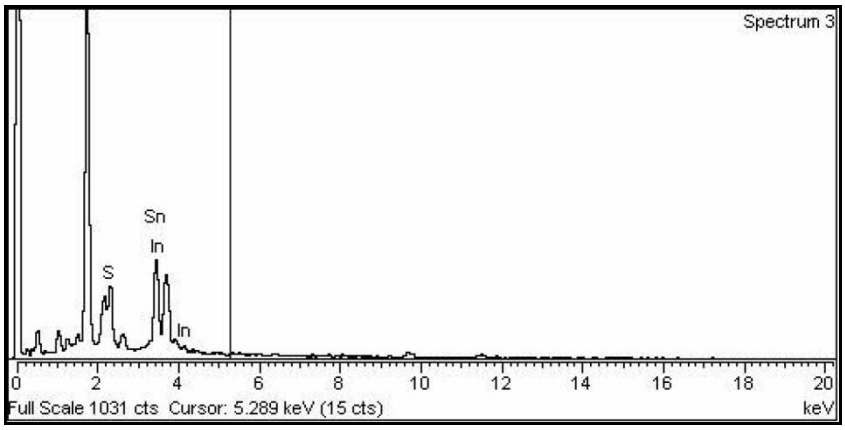

Figure 4 (c)EDAX spectrum of Indium doped SnS thin film at a concentration of 0.001M

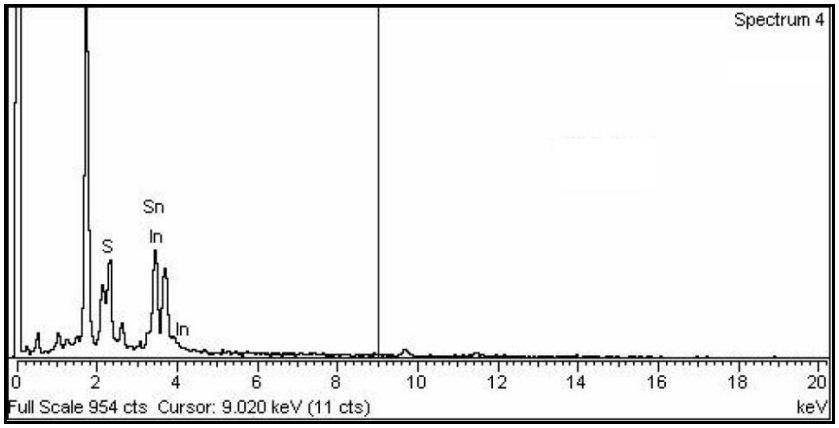

Figure 4 (d)EDAX spectrum of Indium doped SnS thin film at a concentration of 0.01M

Conclusion:

The fabrication of the pure and indium doped SnSthin films on glass substrate were done by spray pyrolysis technique.From the XRD results the structure of the thin films was transformed from orthorhombic to monoclinic and crystalline to the amorphous nature with the increase in doping concentration of indium. The increase in full width at half maximum and hence the reduction in crystallite size determined from XRD results was in agreement with the obtained grain size determined from SEM images. From the EDAX spectrum the presence of indium in the doped thin films and its atomic percentage increased as the doping precursor concentration increased was visualized.

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