Engineering Structural and Opto-Electronic Properties of SnS Films Deposited using Chemical Spray Pyrolysis Technique by Controlling pH of the Precursor Solution

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Abstract

Role of pH of the precursor solution on structural, morphological, electrical and optical properties was investigated, for SnS films prepared using chemical spray pyrolysis (CSP) technique. From the study we could understand that optimum pH of the precursor solution to obtain device quality SnS thin film is 2. The resistivity of SnS films has been brought down by three orders to $6 \times 10^{-2} \, \Omega \text{cm}$ with considerable enhancement in the crystallinity as well as photosensitivity at this optimum pH. Band gap of the films could also be engineered by controlling the pH of the precursor solution. Arrangement of needle-like grains in the film turns out to be denser and is evident from SEM analysis.

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Keywords: Chemical spray pyrolysis; photovoltaic; compound semiconductors; thin films; opto-electronic properties; structural properties

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1. Introduction

Thin films have the potential to revolutionise the present cost of photovoltaic devices by eliminating the use of expensive silicon technology that alone accounts for above 50% of total module manufacturing cost [1]. However presently the popular compound semiconductors in the field of thin film photovoltaic devices are CdTe and CIGS (Copper Indium Gallium Selenide), which contain either highly toxic and / or costly elements. The major challenge for the scientists working in the field of thin film solar cells is to find out proper substitutes for such semiconductor materials. Tin sulphide (SnS) is a very promising abundant and eco friendly material, which can be used as an absorber for inexpensive thin film photovoltaic cells; especially since its band gap nestsles between Si and GaAs, which are the pioneering materials in solar energy conversion. The projected theoretical light conversion efficiency from Loferski diagrams for this compound is higher than 24% [2].

In spite of all the theoretical predictions on superior properties of the SnS thin films, the achieved conversion efficiency so far is quite low [3]. The defects and traps present in the SnS film play crucial role in determining the optoelectronic properties of the material [4]. Another major problem of this class of materials is the control over the stoichiometry, i.e., metal to chalcogen ratios. Because of the large difference in the vapour pressures of tin and sulphur, the stoichiometry is generally controlled by means of sophisticated vapour-monitoring techniques [5]. In contrast to physical vapour deposition (PVD) techniques, in CSP technique, ratios of the constituents are directly linked to their concentrations in the spray solution. Moreover, this technique is ideally suited for deposition of large area films with controlled dopant profiles [6-8]. Nearly stoichiometric, single phase SnS thin films for photovoltaic applications have been deposited using CSP technique by optimising several deposition parameters like substrate temperature, molarity and ratio of anionic and cationic precursor solutions [9].

Improving crystallinity and opto-electronic properties without applying any post deposition treatments is very vital for photovoltaic materials to find its application in novel photovoltaic technologies. Not many works have been dedicated to the improvement of electrical conductivity and / or the crystallinity of the films. Though low resistive SnS thin films can be achieved through ex-situ Sn diffusion [10], this process involves prolonged post deposition treatments which are not much attractive from the industrial point of view at large scale production of the device. This paper describes a method to develop highly conducting and crystalline SnS thin films without employing any post deposition treatments.

pH of the precursor solutions is very critical in CSP since it directly affects the reaction cross section of the precursors at the substrate during the pyrolytic reduction and hence may strongly affect the stoichiometry and grain growth [11]. The effect of pH of the precursors on spray pyrolysed SnS thin films has not been studied in detail. In the present work, we investigate the influence of the pH of the precursor solution and in determining the structural, compositional, optical and electrical properties of the films.

2. Experimental details

SnS thin films were deposited on soda-lime glass substrates using CSP technique. The spraying solution contained equal volumes of 0.1 M stannous chloride (SnCl₂·2H₂O) and 0.2 M thiourea (CSNH₂)₂. Total volume of solution was 30 ml and the pH of the as-prepared solution was 0.8. Temperature of the glass substrate was kept at 375 ± 5 °C, while the spray rate was 2 ml/min. Other minute details of the deposition and characterisation of SnS films have been reported elsewhere [4]. The pH was varied from 0.8 to 3.2 by adding 0, 1, 2, 5, 7.5, 10 and 20 ml of 0.1 M NH₄Cl. The samples prepared using these
modified solutions were named as Pristine, pH 1, pH 2, pH 5, pH 7.5, pH 10 and pH 20 respectively.

Thickness and roughness of the films was measured using Stylus profilometer (Dektak 6). Structural analysis was performed employing X-ray diffraction (XRD) using Rigaku (D.Max.C) X-ray diffractometer with CuKα (λ=1.5405Å) beam and Ni filter, operated at 30 kV and 20 mA. All samples were scanned in the range 10° to 60° with a scan speed of 5°/min. Surface studies of the samples were done with the help of scanning electron microscopy (SEM) (JEOL, JSM-840). Operating voltage for SEM measurements was 20 kV and the surface morphology of the samples was compared at 25,000X magnification. Compositional variation of the samples was analysed using energy dispersive X-ray (EDAX) analysis (operated at 25 kV), which is attached with the SEM (JEOL JSM-840). Optical absorption studies were carried out using UV-Vis-NIR (190-2500 nm) spectrophotometer (Jasco V-750 model). Employing Keithley 236 source measure unit, electrical characterisation and photosensitivity measurements were performed by applying an electric field of 1000 V/m to the films. Silver electrodes were coated on the surface of the film on a fixed area with uniform thickness, keeping a distance of 5 mm in between the electrodes for electrical characterisations. For photosensitivity measurements, the samples were illuminated with a halogen lamp (white light) capable of giving intensity of 60 mW/cm² over the sample surface. IR filter and a water column were kept in between the light source and sample to avoid heating of the sample.

3. Results and discussions

The pH of the precursor solution after adding different volumes of NH₄Cl is given in Table 1. All the films deposited were found to have a thickness of around 800 nm irrespective of the pH of the precursor solution. But the root mean square value of roughness of the films measured by the surface profilometer slightly increased from 40 nm to 65 nm with the increase in pH.

Table 1. Amount of NH₄Cl added in the precursor and the corresponding pH

<table>
<thead>
<tr>
<th>Amount of NH₄Cl added</th>
<th>pH of the precursor solution</th>
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<tbody>
<tr>
<td>Pristine</td>
<td>0.5</td>
</tr>
<tr>
<td>2 ml</td>
<td>0.7</td>
</tr>
<tr>
<td>5 ml</td>
<td>1.0</td>
</tr>
<tr>
<td>7.5 ml</td>
<td>1.7</td>
</tr>
<tr>
<td>10 ml</td>
<td>2.0</td>
</tr>
<tr>
<td>20 ml</td>
<td>2.8</td>
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</table>

3.1. Structural analysis

The XRD pattern of the pristine and the pH varied sample are depicted in Fig. 1. All the films contain single phase SnS, crystallised in Herzenbergate orthorhombic structure, with preferential orientation along {1 1 1} plane. Grain size of the films was calculated from the peak at 2θ = 31.53° using the Debye-Scherer formula, \(D = 0.9\lambda/(\beta\cos\theta)\), where D is the diameter of the crystallites forming the film, \(\lambda\) is the wavelength of X-rays (CuKα line), \(\beta\) is the full width at half maximum in radians and \(\theta\) is the Bragg angle. Grain size variation of the samples deposited using precursors with different pH is depicted in Fig. 2. It is evident from Figs. 1 and 2 that the crystallinity of the samples improves with increase in the pH of the precursor till an optimum value of pH and thereafter, it starts deteriorating with further increase in pH. The sample pH 7.5 is found to be most crystalline.
3.2. Optical properties

$(\alpha h \nu)^2$ versus $h \nu$ plot of the pH varied samples is given in Fig. 3. The band gap of the films decreased slightly till sample pH 7.5 and further increase in the pH resulted in films with higher band gap. The reduction in band gap till the optimum pH value could be due to the improvement in crystallinity of the films.
3.3. Morphological and compositional analysis

Figure 4 shows the SEM image of the pristine and the pH varied samples. All the films were uniform without any pin holes or cracks, and having an interesting ‘needle like’ grain structure. SEM micrographs clearly indicated an increase in the density of the grains as we move from the pristine sample to sample pH 20 without much enhancement in the grain size.
Figure 5 shows the variation in atomic percentage of Sn, S and Cl with respect to pH of the precursor solution as obtained from EDAX measurements. Variations in atomic percentage of Sn and Cl show an interesting ‘mirror like’ resemblance. This may be due to ‘Charge Compensation’ mechanism (as Cl goes into S site, there is a reduction of a negative charge and Sn concentration should accordingly get reduced to compensate this). It is evident from Fig. 5 that pristine film is almost stoichiometric and on increasing pH of the precursors, the films initially become slightly ‘S’ rich. But at still higher pH, a retracing effect is observed, eventually making sample pH 20 again nearly stoichiometric.

![Graph showing variation in atomic percentage of Sn, S and Cl with respect to pH](image)

**Fig. 5.** EDAX of the films prepared at different pH: Plot showing variation in atomic percentage of Sn, S and Cl with respect to pH of the precursor solution.

### 3.4. Electrical conductivity studies

The variation in resistivity and photosensitivity of the samples is depicted in Fig. 6. Resistivity of the samples decreased with increase in pH of the precursor solution till sample pH 7.5; however further increase in pH resulted in slight increase of resistivity. Resistivity of sample pH 7.5 was found to be almost three orders less than that of the pristine sample. This value is assumed to be the lowest resistivity ever reported for SnS thin films. Interestingly the photosensitivity of the material, (defined as the ratio of increase in conductivity on illumination to the dark conductivity), exhibited an anomalous behaviour with pH variation. Photosensitivity was maximum for the lowest resistive sample. The correlation between the crystallinity and photosensitivity indicates that grain boundaries in SnS films do not favour the lifetime of the photogenerated carriers, unlike in CuInSe$_2$ films reported earlier [12]. Similar observation has been reported earlier for SnS films upon ex-situ Sn diffusion as well [10]. Usually, higher photo sensitivity correlates to higher resistivity due to the fact that carriers that are easily photogenerated, are vulnerable to sudden recombination as well, and the dark resistivity is higher for such samples. But this type of photosensitivity is not useful for photovoltaic applications, since the lifetime of the carriers is too short to
be efficiently separated. However, the photosensitivity in the samples studied here is due to enhancement in crystallinity, which makes them very useful in photovoltaic device applications.

![Graph showing variation in Resistivity and Photosensitivity with pH](image)

Fig. 6. Plot showing variation in Resistivity and Photosensitivity of the samples with pH of the precursor solution

Sn vacancies in SnS films are reported to be the cause for acceptor levels and hence the p-type conductivity of SnS thin films [13]. The EDAX measurements clearly revealed that, as the pH increases, the material is becoming deficient in Sn concentration, which can increase the defect level densities due to Sn vacancies, providing more carriers and thus enhances the conductivity. So it may be due to the creation of such Sn vacancies, that the acceptor level concentration increases and the material becomes more conducting. However as the pH goes above the optimum value (pH = 7.5), the resistivity increases since Sn concentration is also increased after the optimum pH. Main advantage of the present study is that films with this superior property are achieved without employing any post deposition treatments.

4. Conclusions

The significance of pH of the precursor solution in determining the structural, morphological and optoelectronic properties of the SnS film prepared using CSP technique has been investigated in this manuscript. It is observed that the crystallinity of the films has a definite correlation with pH of the precursor solution, and an optimal pH exists for the optimal crystallinity. The band gap of the films can also be engineered by controlling the precursor’s pH. Moreover we could obtain a drastic reduction in the resistivity of the SnS films through this study and the resistivity value obtained for the optimum pH sample is the lowest reported so far for the material. The lowest resistive film exhibit the maximum photosensitivity among the set. Most importantly, these superior properties are achieved without employing any post deposition treatments and hence it is quite useful for the development of low-cost thin film photovoltaic technology.
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References