Investigations on the Properties of Nanostructured Mg-Doped Sn$_2$S$_3$ Thin Films towards Photovoltaic Applications

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This paper reports the synthesis, crystal structure, surface morphology, optical and electrical properties of Mg-doped Sn$_2$S$_3$ thin films deposited by spray pyrolysis technique. All the films exhibit orthorhombic crystal structure with a (211) preferential orientation. Crystal size calculations based on the Debye–Schererr formula indicated that the Sn$_2$S$_3$ crystallite size increases with Mg content from 27.97 nm to 33.58 nm. Scanning electron microscopy images showed that all the films were very smooth composed of nanoneedle and nanoplate shaped grains. The band gap energy of the films exhibits a blue shift from 1.94 eV to 2.09 eV with increase in Mg concentration. Resistivity values of the undoped and Mg-doped Sn$_2$S$_3$ films were found to be in the order of 0.1 Ωcm. From the obtained results it is observed that the Sn$_2$S$_3$ film coated with 2 wt% Mg concentration exhibits better physical properties.

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1. Introduction

Tin sulphide, a chalcogenide compound belonging to a family of IV–VI semiconductors have attracted attention in recent decades due to its numerous applications. Its band gap varies in the range of 0.8–3.5 eV [1, 2] which make it suitable as an absorber or window layer in photovoltaic solar cells. Tin sulphide has three main phases of which SnS$_2$ and SnS exhibit layered structure whereas Sn$_2$S$_3$ exhibit ribbon-like structure [3]. Sn$_2$S$_3$, a material with electron lone pairs is a mixed valence Sn compound which crystallizes in orthorhombic crystal structure [4]. Sn$_2$S$_3$ is a direct forbidden semiconductor with a band gap of 0.95 eV and high anisotropic conduction [5], which makes it suitable as $p$–$n$ or $p$–$i$–$n$ structures in photovoltaic applications [6]. Sn$_2$S$_3$ could also be used to prepare near-lattice–matched heterojunctions such as Sn$_2$S$_3$/CdTe, Sn$_2$S$_3$/GaSb, Sn$_2$S$_3$/AlSb, etc, for applications in the detection and generation of infrared radiation [7].

Due to the existence of numerous particle boundaries, Sn$_2$S$_3$ films have low electron-transport efficiency, which would result in easy recombination of electrons and holes thereby limiting the efficiencies of Sn$_2$S$_3$ based solar cells. It has been proposed recently that in 3D nanostructured networks comprised of semiconductor nanorods, nanotubes or nanowires high electron transport rate could be achieved, as these networks provide direct conduction pathways for rapid collection of photo-generated electrons [8]. In photoelectric conversion, these 3D networks can enhance relaxation light harvesting by multiple scattering thereby increasing the conversion efficiency [9]. Sn$_2$S$_3$ is one such material which exhibit 3D nanostructured network depending on the preparation conditions.

Sn$_2$S$_3$ thin films have been prepared earlier by various techniques such as spray pyrolysis [10], chemical bath deposition [11], potentiostatic electrodeposition [12], etc. Among these techniques, spray pyrolysis is a promising technique for preparing semiconducting thin films suitable for energy conversion applications. The conductivity and carrier concentration of Sn$_2$S$_3$ films deposited by spray pyrolysis technique have been estimated about $4.35 \times 10^{-3}$ (Ωcm)$^{-1}$ and $9.4 \times 10^{14}$ cm$^{-3}$, respectively. It has been reported earlier that the resistivity of Sn$_2$S$_3$ is affected by the increased number of grains possessed by it [13]. Also Sn$_2$S$_3$ films with tin vacancies show $p$-type conductivity, while the films with sulphur vacancies show $n$-type conductivity [14]. In Sn$_2$S$_3$, carrier type might be subject to change as its carrier concentration is sensitive to the growth or annealing conditions as the formation energies of the tin and sulphur vacancy defects are close in energy.

In photovoltaic applications, mixed type of Sn$_2$S$_3$ would be detrimental to its transport properties which would lower the device performance. Therefore, in order to improve the photovoltaic device performance, single phase Sn$_2$S$_3$ is essential which can be achieved by controlling the Sn and S vacancies. However, the for-

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(15)
The deposition of p-type Sn₂S₃ is very difficult because of strong self-compensation effect due to sulphur vacancies and the depth of the acceptor level. To form a single phase Sn₂S₃ of p-type, it is essential to control the self-compensation effect due to sulphur vacancies which can be achieved through doping.

Magnesium is a transition metal element belonging to $P63/mmc$ space group. Mg$^{2+}$ has an ionic radius of 0.72 Å which is small compared to that of Sn$^{2+}$ (0.93 Å). Therefore, doping of Mg in Sn₂S₃ permits its band gap to be tailored and also Mg doped Sn₂S₃ leaves the lattice constants almost invariant due to the high solid solubility of MgS in Sn₂S₃. Also Mg metal based sulphide thin films exhibit p-type conductivity. Therefore, it is expected that when MgS is alloyed with Sn₂S₃, it may be possible to form a single phase of Sn₂S₃ with p-type. Motivated by this fact, in this work Mg-doped Sn₂S₃ films were prepared by spray pyrolysis technique with different concentrations of Mg (0, 1, 2, and 3 wt%) and the effect of Mg doping on the properties of Sn₂S₃ films was investigated and the results are reported here.

### 2. Experimental details

Sn₂S₃ films were deposited by spray pyrolysis technique using tin(II) chloride, (SnCl₂·H₂O) (0.02 M) and thiourea CS(NH₂)₂ (0.02 M) as precursor salts. First SnCl₂ is dissolved in a mixture of HCl and deionized water in the volume ratio of 1:5 (in total 30 ml volume) while thiourea was added to this solution and stirred well for 30 min. To achieve Mg doping, MgCl₂ is used as the precursor salt. Mg concentration is varied in the starting solution as 0, 1, 2, and 3 wt%. The resultant solution was activated by this fact, in this work Mg-doped Sn₂S₃ films were deposited by spray pyrolysis technique with different concentrations of Mg (0, 1, 2, and 3 wt%) and the Sn₂S₃ film coated with 2 wt% Mg concentration was found to have maximum crystallite value of 33.58 nm confirming its improved crystallinity.

### 3. Results and discussion

#### 3.1. XRD analysis

Figure 1 shows the XRD patterns of Mg-doped Sn₂S₃ thin films coated with 0, 1, 2 and 3 wt% Mg concentrations. All the films exhibit a well defined peak at about 31.71° and a weak peak at 66.26° corresponding to the (211) and (422) planes of orthorhombic structure (JCPDS card No. 75-2183). Besides these peaks, no extra peaks corresponding to any phase of tin sulphide were observed confirming that the as deposited films were of Sn₂S₃ phase only. It is observed that the peak intensity of the (211) plane increased with increase of Mg content attaining a maximum value for the film coated with 2 wt% doping concentration indicating better crystallinity of this film. The crystallite size $D$ of the Mg-doped Sn₂S₃ films was calculated from the Scherrer formula [15]:

$$D = \frac{0.9\lambda}{\beta \cos \theta},$$

where $\lambda$ is the wavelength of the X-ray (1.5406 Å), $\beta$ is the full width at half maximum and $\theta$ is the Bragg angle.

The calculated crystallite size values increases with doping concentration and the Sn₂S₃ film coated with 2 wt% Mg concentration is found to have maximum crystallite value of 33.58 nm confirming its improved crystallinity.

### Table I

<table>
<thead>
<tr>
<th>Mg [wt%]</th>
<th>2θ(211)</th>
<th>$D$ [nm]</th>
<th>$\varepsilon \times 10^{-3}$</th>
<th>Lattice parameters [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>31.706</td>
<td>27.97</td>
<td>1.2390</td>
<td>5.641</td>
</tr>
<tr>
<td>1</td>
<td>31.856</td>
<td>30.82</td>
<td>1.1244</td>
<td>5.619</td>
</tr>
<tr>
<td>2</td>
<td>31.892</td>
<td>33.58</td>
<td>1.0320</td>
<td>5.612</td>
</tr>
<tr>
<td>3</td>
<td>31.880</td>
<td>32.88</td>
<td>1.0539</td>
<td>5.614</td>
</tr>
</tbody>
</table>

It is observed from the XRD patterns that the 2θ value of the (211) plane of the Sn₂S₃ films shifts towards higher Bragg angle (Table I) with increase in Mg concentration.
inferring a contraction in their lattice volumes. The calculated lattice parameter values of the Mg-doped Sn$_2$S$_3$ thin films decreases with increase in Mg concentration which infer that Mg$^{2+}$ ions have substitutionally replaced Sn$^{2+}$ ions in the host lattice. This inference is arrived as the ionic radius of Mg$^{2+}$ (0.72 Å) is smaller than Sn$^{2+}$ (0.93 Å).

The strain in the film was calculated using the relation [16]:

$$\varepsilon = \frac{\beta \cos \theta}{4}. \quad (3.2)$$

The obtained values decreases with increase in Mg concentration and the film coated with 2 wt% Mg concentration exhibited a low value of strain confirming its improved crystallinity.

### 3.2. SEM analysis

Figure 2a–d shows the SEM images of Mg-doped Sn$_2$S$_3$ thin films. It is observed that the surface of pure Sn$_2$S$_3$ film is smooth and dense composed of nanoneedle shaped grains (Fig. 2a). For 1 wt% Mg dopant, the film surface seems to be tightly packed with a mixture of needle shaped and plate-like grains (Fig. 2b). As the Mg concentration is increased further, the surface gets modified with equally sized nanoneedles for the film coated with 2 wt% Mg concentration (Fig. 2c). With further increase in Mg concentration, the surface gets modified with equally sized plate like grains along with few nanoneedles for the film coated with 3 wt% Mg concentration (Fig. 2d). These results infer that Mg doping strongly influences the surface morphology of pure Sn$_2$S$_3$ film and it is observed that the film coated with 2 wt% Mg concentration exhibits better morphology supporting the results obtained in XRD analysis.

### 3.3. Electrical studies

The electrical resistivity values of the films measured by two point probe setup are compiled in Table II. The resistivity values of the films are found to be in the range of $10^{-1}$ Ωcm. The resistivity range obtained here exactly matched with earlier reports [17]. It can be observed that film resistivity decreases with increase in Mg concentration, attaining a minimum value of $1.13 \times 10^{-1}$ Ωcm for the film coated with 2 wt% Mg concentration. The decreased resistivity values observed with Mg doping might be due to increased crystallite size or decreased lattice strain and improved crystallinity. The reduction in resistivity with Mg doping might also be due to increased carrier concentration which might have occurred due to substitutional incorporation of Mg$^{2+}$ ions into the host lattice.

<table>
<thead>
<tr>
<th>Mg [wt%]</th>
<th>$E_g$ [eV]</th>
<th>$E_u \times 10^{-2}$ [eV]</th>
<th>$\rho \times 10^{-1}$ [Ωcm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.94</td>
<td>3.28</td>
<td>5.81</td>
</tr>
<tr>
<td>1</td>
<td>2.09</td>
<td>3.19</td>
<td>3.69</td>
</tr>
<tr>
<td>2</td>
<td>2.04</td>
<td>3.10</td>
<td>2.62</td>
</tr>
<tr>
<td>3</td>
<td>2.04</td>
<td>3.10</td>
<td>2.62</td>
</tr>
</tbody>
</table>

### 3.4. Optical studies

Figure 3 shows the optical transmittance spectra of undoped and Mg-doped Sn$_2$S$_3$ thin films recorded in the wavelength range of 300–1100 nm. The average transmittance of the Mg-doped Sn$_2$S$_3$ films decreases with increase in the Mg content which may be due to increased absorption by free carriers [18]. It is also observed that the absorption edge of the doped films shift towards lower wavelength side which indirectly indicate an increment in their band gap values. In semiconductor materials, optical transitions take place by direct and indirect transitions. The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the optical band gap $E_g$ of Mg-doped Sn$_2$S$_3$ films. The band gap values can be obtained from the optical absorption spectra by the relation [19]:

$$a h \nu = A(h \nu - E_g)^n, \quad (3.3)$$

where $\alpha$ is the absorption coefficient, $h \nu$ is the photon energy, $n$ assumes the values 1/2, 2, 3/2, and 3 for allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively. $A$ is a constant related to the extent of band tailing. The band gap values were determined by extrapolating the linear portion
The Urbach tail, the width of the localized states available in the band gap region of thin films, affects their band gap structure and transitions [21]. The Urbach tail of the Mg-doped SnS\textsubscript{3} thin films was determined by the relation [22]:

$$\alpha = \alpha_0 \exp \left( \frac{E}{E_u} \right),$$  

(3.4)

where $E$ is the photon energy, $\alpha_0$ is constant and $E_u$ is the Urbach energy which refers to the width of the exponential absorption edge. The $E_u$ values of the Mg-doped SnS\textsubscript{3} thin films were calculated from the slopes of the plots between $\ln(\alpha)$ vs. $h\nu$ (Fig. 5), and the obtained $E_u$ values increase in Mg concentration supports for the improved crystallinity of the doped films, which means that there are only minimum number of defects in the SnS\textsubscript{3} film structure even after doped with Mg. It is also observed that both $E_g$ and $E_u$ values vary in opposite ways. The low value of $E_u$ observed for the SnS\textsubscript{3} film coated with 2 wt\% Mg concentration for which $E_g$ is maximum confirm the minimization of defects in this film which favours for its improved crystalline nature.

### 3.5. PL studies

Photoluminescence (PL) spectrum provides information on the optically active defects and relaxation pathways of excited states. Information regarding the point defects present in thin films such as vacancies, interstitials and impurities can be obtained from PL studies [23]. Figure 6 displays the PL spectra of the undoped and Mg-doped SnS\textsubscript{3} (Mg doping levels: 2 and 3 wt\%) thin films, excited at $\lambda = 400$ nm. It is observed that all the films exhibit emission peaks at 485 nm (2.56 eV), 544 nm (2.28 eV) and 608 nm (2.04 eV). The peak at 485 nm can be attributed to the transitions of trapped electrons from donor levels to the valence band which can be assigned to defect states, probably S vacancy states [24]. The green band emission observed at 2.28 eV has been originated from the transition of the increased...
$V_s$ donors to recombine with S interstitials ($I_s$) acceptors in the valence band [25]. The yellow band emission observed at 2.04 eV is caused by a donor–acceptor pair [26]. Ahmad-Bitar [27] reported a similar band for CdS thin films which they attributed to recombination via surface localized states, a transition from cadmium interstitial ($I_{Cd}$) to valence band, and the transition from interstitial cadmium–cadmium vacancy complex $I_{Cd}^+V_{Cd}^-$ which acts as a donor to an acceptor level.

![PL spectra of Mg-doped Sn$_2$S$_3$ thin films.](image)

4. Conclusion

Nanostructured pure and Mg-doped Sn$_2$S$_3$ thin films were prepared by spray pyrolysis technique. The effect of Mg doping on the structural, morphological, optical and electrical properties of Sn$_2$S$_3$ films were investigated. XRD studies revealed that all the films exhibited orthorhombic structure with a preferential orientation along the (211) plane. The 2θ angle of the (211) peak was found to be shifted towards higher Bragg angle with increasing Mg content in the films. Crystallite size increased from 27.97 nm to 33.58 nm with increase in Mg concentration. The presence of nano needles in the films is evinced from the SEM images. Optical band gap was blue shifted with doping. Urbach energy decreased with increasing Mg concentration confirming the decrement in the disorderliness of the films with doping. Film coated with 2 wt% Mg concentration exhibited a minimum resistivity of $1.13 \times 10^{-1}$ Ωcm. From the obtained results, it was confirmed that the Sn$_2$S$_3$ film coated with 2 wt% Mg concentration exhibited better physical properties which make them suitable for photovoltaic applications.

References