Parameters influencing the optical properties of SnS thin films

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Abstract: Tin sulphide (SnS) thin films have been recognized as a potential candidate for solar cells. Many fabrication techniques have been used to grow SnS thin films. The band-gap, $E_g$ of SnS films as reported in literature, were found to vary from 1.2–2.5 eV depending on the film fabrication technique. The present work reports the structural, compositional, morphological and optical characterization of SnS thin films fabricated by thermal evaporation at room temperature. Results show that for the given fabrication technique/condition, the band-gap functionally depends on the lattice parameter and grain size. The well-defined variation allows for tailoring SnS film as per requirements.

Key words: nano-composites; nanostructures; photoluminescence; oxides

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1. Introduction

Tin Sulphide (SnS) is formed from elements belonging to the IV–VI group of the periodic table[1]. Like other sulphide compounds (As$_2$S$_3$ and Sb$_2$S$_3$ etc.), SnS also attracted attention in the 1970 and 1980’s for possible application as an optical storage medium[2, 3]. However, recent investigations are directed towards studying its potential as a photovoltaic or solar cell essentially due to its high absorption coefficient, low cost and low toxicity[4-5]. A pertinent point is that both applications require SnS to be in its thin film state. Being a layered chalcogenide[6-7] of relatively low melting point[8], SnS has been found to be a suitable candidate for thin film fabrication. Depending on film thickness, the color of SnS films varies from orange to brown when viewed in transmission. Thus, during the last 30–40 years there has been substantial work on the fabrication of SnS thin films using various methods like thermal evaporation[9], RF sputtering[10], chemical vapor deposition[11], electrodeposition[12], and spray pyrolysis[13]. The reported optical band-gap of SnS films lies between 1.1–2.1 eV[14, 15] depending on the fabrication method used.

While there are large number of reports on SnS, more systematic studies should be undertaken considering its potential commercial application as a solar cell. Especially to understand why the band-gap of SnS varies so much. With this intention, we have carried out systematic studies on SnS thin films of varying thicknesses grown by thermal evaporation. The structural, morphological, compositional and optical properties of the films are reported here. The role of the intra-planar forces in the structured layer (as seen from the lattice parameters of unit cells within the nano-crystalline SnS grains) and the grain size on the band-gap of the films have been discussed.

2. Experimental

SnS thin films of varying thickness were grown on glass substrates maintained at room temperature by thermal evaporation at vacuum better than $\sim 4 \times 10^{-5}$ Torr. A Hind High Vac (12A4D), Bengaluru thermal evaporation coating unit was used for the thermal evaporation process. SnS powder of 99% purity supplied by Himedia (Mumbai) was used as the starting material. The thicknesses of the as-grown films were then measured by a Veeco Dektak surface profiler (150). The standard structural, morphological and optical characterization of the films were done using a Bruker D8 diffractometer (in the $\theta$–$2\theta$ mode), Renishaw Invia Raman microscope, field-emission scanning electron microscopy (FE-SEM FEI-Quanta 200F) and a systronics UV-VIS double beam spectrophotometer (2202). Chemical composition of the films were determined using Kratos Axis Ultra DLD’s X-ray photoelectron spectroscopy (XPS) with an Al k$\alpha$ target.

3. Results and discussion

3.1. Structural studies

The X-ray diffractograms of very thin SnS films (thickness less than 150 nm) were unmarked with a hump between $(2\theta \approx) 10^\circ$–$60^\circ$. The absence of peaks suggests that the samples were not crystalline. This is not surprising since chalcogenides grown at room temperature are usually amorphous in nature. However, the hump indicates that there might be some short range order among the atoms. As the sample thickness increases (270 nm and above), a small diffraction peak emerges on the hump around $2\theta \approx 31^\circ$. Thus, it would appear that ordering increases with increasing film thickness. Figure 1(a) shows the X-ray diffraction patterns of samples of different thicknesses. The peak positions matched with those reported in ASTM Card No. 83-1758 implying an orthorhombic unit cell structure with lattice parameters of 4.148, 11.48 and 4.177 Å. The standard relationship[18] was used to determine the lattice parameters using the peak positions

$$\sin^2 \theta_i = Ah_i^2 + Bk_i^2 + Cl_i^2.$$
Fig. 1. (a) X-ray diffraction pattern of SnS films of various thicknesses. The sample thicknesses and Miller indices are also indicated. (b) Variation in lattice parameters with film thickness. Names and peak Miller indices are indicated.

Fig. 2. TEM micrograph of a 480 nm thin film shows the layered structure of SnS thin film.

Fig. 3. The average grain sizes of SnS films were found to be linearly proportional to the film thickness.

The lattice parameters $b$ and $c$ were found to be $11.39 \pm 0.01$ Å and $4.117 \pm 0.002$ Å respectively. The lattice parameters were found to remain constant with increasing film thickness within experimental error (Fig. 1(b)). Figure 1(b) however, shows an initial decreasing trend of lattice parameter $a$ with increasing film thickness. However, for film thicknesses greater than 600 nm, there is no tensile stress acting on the films and $a$ remains constant.

Figure 2 is a transmission electron microscope (TEM) image of a 480 nm thick film. The image clearly shows the layered nature of the SnS films. The interplanar distances were found to be 2.45 Å ($\approx b/4$). This would mean the films are oriented with the (040) plane lying parallel to the substrate. The oriented nature of the films is also seen in the XRD patterns with the (040) peak standing out as the most intense peak in agreement with observations reported[16, 17]. The X-ray diffraction peak’s full width at half maximum (FWHM) gives the grain size using the Scherrer formula[18]. Figure 3 shows a linear relationship between the average grain size and film thickness.

3.2. Raman spectra and XPS analysis

The Raman spectra of SnS thin films were collected using an Argon laser in back scattering mode. The laser power (15 mW), exposure time (30 s) and beam area were maintained constant for all the samples. Since SnS is known to show changes induced by the photo-thermal absorption of light[2, 3], all the Raman spectra were collected using a low power laser. The nano-crystalline samples showed three prominent peaks which were consistently present in all the samples (Fig. 4) in varying proportions around $\sim 170$, $\sim 230$ and $\sim 330$ cm$^{-1}$. However, each sample showed slight displacement in peak position compared to those reported for single crystal Raman peaks[6]. The consensus in literature is that the 330 cm$^{-1}$ peak indicates the existence of SnS$_2$[19]. This may have resulted due to the growth technique, since the starting material’s Raman spectrum does not exhibit a peak at 330 cm$^{-1}$. The SnS$_2$ contribution decreases with thickness as is evident from the decreasing 330 cm$^{-1}$ peak intensity and area with increasing film thickness.
Fig. 4. Raman spectra of SnS thin films of various thicknesses show existence of three prominent peaks at 170 cm\(^{-1}\), 238 cm\(^{-1}\) and 330 cm\(^{-1}\) (Refer to the text).

Fig. 5. XPS peaks of tin and sulphur for 270 and 600 nm thick films are visibly different. The 270 nm sample’s XPS peaks can be deconvoluted into two peaks, indicating presence of SnS (major contribution) and SnS\(_2\) (minor contribution). The peaks from SnS\(_2\) are absent in the 600 nm sample, thus showing thicker films are of SnS. This was also confirmed by chemical composition analysis done on the films of different thicknesses using X-ray photoelectron spectroscopy (XPS). Figure 5 compares the XPS peaks of sulphur and tin for 270 and 600 nm thicknesses. The 600 nm thick sample had lone sulphur 2p and tin 3d\(_{5/2}\) peaks that could not be deconvoluted. The number of sulphur (\(n_S\)) and tin atoms (\(n_{Sn}\)) in bonding per cm\(^2\) area can be evaluated using the area under the curve (\(\Delta\)) and cross-sectional values (\(\sigma\))\(^{[20]}\) in the standard formula\(^{[21]}\)

\[
\frac{n_S}{n_{Sn}} = \frac{\Delta_S \sigma_{Sn}}{\sigma \Delta_{Sn}}.
\]

The ratio of sulphur to tin in this sample was found to be \(\approx 0.9\), suggesting within experimental error that the 600 nm sample is of SnS. However, in comparison with this, the 270 nm sample’s sulphur (2p) and tin (3d\(_{5/2}\)) peaks can be deconvoluted into two peaks. Based on the Raman results, we associate the major peaks with SnS and the minor ones with SnS\(_2\). Using the above mentioned formula and the area under the curves, the ratio of S/Sn from the major peaks give 1.1 while from the minor peaks S/Sn \(\approx 1.9\). Thus, thin samples (270 nm and 480 nm) have both species of SnS and SnS\(_2\). From the ratio of the two tin peaks, we may say only 10%-12% of the film is SnS\(_2\).

The 170 cm\(^{-1}\) peak or the B\(_{2g}\) peak is associated with interaction along the inter-layer b axis\(^{[22]}\) while the 238 cm\(^{-1}\) peak is the symmetric Sn–S bond’s stretching mode (A\(_g\))\(^{[23]}\). As the film thickness increases, the position of these two peaks shifts (Fig. 6 shows the variation). Initially, the peak position of A\(_g\) was found to decrease with increasing film thickness, however, after 600 nm the peak position remained fixed \(\approx 226\) cm\(^{-1}\). The region of saturation corresponds to where samples have constant lattice parameters. Hence, we believe that the peak position of A\(_g\) is intimately related to the lattice size. A plot between A\(_g\) and ‘a’ (Fig. 6(a)) confirms a linear relation between the two. An increase in wave-number (vibration frequency) marks the increase in restoring force (bond strength). Hence, the results suggest that increasing tensile stress along ‘a’ direction is accompanied with increased restoring force acting between the tin and sulphur atom.

Fig. 6. Variation of Raman peak positions with film thickness. Both B\(_{2g}\) and A\(_g\) show a decreasing trend with film thickness. However, A\(_g\) levels out for film thicknesses above 600 nm (the curve looks similar to that of Fig. 1(b)).

Variation in grain size seems to effect “inter-planar”
Fig. 7. (a) $A_g$ peak position is found to depend on the lattice parameter $a$. (b) $B_{2g}$ peak position shows dependence on grain size.

Fig. 8. Scanning electron micrographs (SEM images) of SnS thin films of thicknesses. (a) 150 nm. (b) 480 nm. (c) 600 nm. (d) 900 nm.

distances, thus effecting the $B_{2g}$ peak position. Increased grain size is accompanied with lower Raman wave-numbers and hence indicate lower restoring forces, which from our above analysis on $A_g$, would imply lattice constant $b$ would decrease with increasing grain size. However, the variation in $b$ (1.41–11.37 ± 0.01 Å) as seen from X-ray diffraction results) is too small to justify this comment.

3.3. Morphological studies

Figure 8 shows representative SEM images of SnS as-grown films of different thicknesses, namely 150, 480, 600 and 900 nm. The grain morphologies are similar to those reported earlier[31]. In the case of the thicker films (480, 600 and 900 nm), the morphology of the films appear very similar to each other, with a noticeable increase in grain density with increasing film thickness. However, the morphology of the 150 nm thick film is distinctly different consisting spherical grains. As discussed above, Raman spectra (Fig. 4) and XPS analysis clearly shows that this sample contains SnS$_2$. This should explain the distinctly different morphology of this sample from the remaining samples. Though results related to this sample have not been used in this present study, we have included its SEM to show that very thin films are dominated by SnS$_2$ marked with spherical grains. Grains of these morphology are absent in samples with thicknesses greater than 250 nm, highlighting that there is no or negligible contribution by SnS$_2$ in these samples.

Fig. 9. Graph shows the variation in band-gap with grain size for as grown SnS thin films. The filled circles represent samples that have the same lattice parameters while unfilled circles represent samples with varying grain size and lattice parameter. The solid curve is the best fit of Eq. (1) to the data points. The fit suggests band-gap variation is a result of the electron’s quantum confinement within the grain.

3.4. Optical studies

The absorption spectra of as-grown SnS films with varying thicknesses were obtained between 300 and 1100 nm at room temperature. The band-gaps were evaluated using the absorption coefficient $\alpha$ obtained from the UV–visible spectra using standard formula[32]

$$\alpha = \frac{2.303 A}{t},$$

where $A$ and $t$ are the film’s absorbance and thickness respectively. The band-gap of the films can be evaluated from this information. SnS is reported to have both an indirect[15] and a direct band-gap[33]. Band-gaps are usually evaluated using Tauc’s method[34] where a graph between $(\alpha h\nu)^n$ is plot with respect to $h\nu$. The linear region of this plot is extrapolated to intersect the ‘$x$’-axis at $y = 0$. The point of intersection gives the band-gap of the material. For direct allowed transitions, the absorption coefficient is related to the photon energy by the following equation[35–38]

$$(\alpha h\nu)^2 = K(h\nu - E_g),$$

where $K$ is the proportionality constant. Figure 9 shows the variation of the band-gap with grain size. The 270 and 480 nm thin films have a considerably large band-gap. While one may suspect this to be due to the existence of SnS$_2$ in these samples, it should be noted that only 10% of the sample is SnS$_2$. They are predominantly SnS films. Also, the linear trends shown in Fig. 7(a) and (b) argue that little or no significant contributions are made by SnS$_2$. We hence shall assume the large energy band-gaps to be manifestations of the structural and morphological trends of SnS. Before commenting on this however, notice the nature of band-gap variation with grain size. Experimental data fits to

$$E_{g\text{nano}} = E_{g\text{bulk}} + \frac{\hbar^2\pi^2}{2Mr^2},$$

where $r$ is the radius of the nanoparticle and $M$ the effective mass of the system. In other words, the band-gap is inversely
proportional to the grain size. This fit suggests quantum confinement of the electrons\(^{[39]}\). Note that the data points represented by unshaded circles in Fig. 9 have different \(a\) lattice parameters. Figure 10 uses the same data points of Fig. 9, but in three dimensions. We can now see the band-gap dependence on both grain size and lattice parameter. Mathematically, the band-gap of SnS nano-crystalline thin films is a two variable function of grain size and lattice parameter, \(E_g(a, r)\). While the relation between the band-gap and grain size is a well known (Eq. (1)), there is no known relation between the band-gap and lattice parameter \((a)\). Hence, more studies would be required to establish the observed two variable dependency.

**Conclusion**

Tin sulphide films grown on glass substrates at room temperature by thermal evaporation were found to be nanocrystalline in nature for thicknesses more than 270 nm. X-Ray diffraction shows that the grain size increased linearly with film thickness. Diffraction studies and electron microscope images show that the atoms of SnS are arranged in an layered and oriented manner with ortho-rhombic structure and residual tensile stress acting along the \(a\) axis. The films had direct band-gaps ranging from 1.8 to 2.1 eV depending on the grain size and lattice parameter. Thus, the study reveals that the band-gap of SnS is a two variable function, which can be tailored as per requirements by controlling the grain size and lattice parameters.

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