Suitability of SnS thin films for photovoltaic application due to the existence of persistent photocurrent

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Received 22 April 2015, revised 9 September 2015, accepted 22 October 2015
Published online 16 November 2015

Keywords nanocrystalline materials, photocurrent, semiconductors, thin films

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Tin sulfide (SnS) is a layered compound that retains its structure when deposited as thin films by thermal evaporation. The films thus obtained were found to have p-type conductivity, as confirmed by the hot-spot method. The films were found to have oriented growth with the direction of orientation changing with film thickness. The film’s morphology was also found to change with orientation. The poor conductivity of the thicker samples made it difficult to make photoconductivity characterization, however, unlike reported studies in the literature, the thinner samples showed photosensitivity to be defect dependent and independent of film thickness and grain size with a high-persistent photocurrent. With their absorptivity, photosensitivity, optimum bandgap, and traps within the bandgap giving the charge carriers a longer lifetime, thin samples of tin sulfide give adequate scope for designing efficient photovoltaics.

1 Introduction

The search for an abundant, inorganic and nontoxic material, with a good absorption coefficient at relatively low thicknesses in solar-cell applications has narrowed down to tin sulfide (SnS) [1, 2]. SnS has been successfully fabricated by chemical methods [3, 6], spray pyrolysis [7, 9], sputtering [10], thermal evaporation [2, 11, 13], and electron-beam-assisted evaporation [14]. The bandgap of the films were reported to lie between 1.3–2.5 eV [1, 15, 18] depending on the fabrication technique. With the bandgap lying in this range, SnS is capable of utilizing the visible range of solar radiation falling on the earth’s surface.

The literature shows that the present efforts are directed toward finding an appropriate second layer for the diode formation with SnS. The best efficiency reported is 4.4% with zinc oxysulfide, Zn(O,S), acting as the n-layer [19]. Annealing [20] and/or sulfurization [21] of the SnS layer has also been suggested to improve the SnS solar-cell efficiency. However, directed fundamental characterization of SnS films especially on persistent photoconductivity is absent. In fact a search of the literature only shows a couple of articles on SnS persistent photoconductivity [22, 23]. Considering that a long carrier lifetime (in relation to photoconductivity) would assist in improving the photovoltaic performance [24], an in-depth correlation of carrier lifetime with film parameters is a must. We have tried to address this in the present work.

The present work reports the fabrication of p-type SnS thin films via a thermal evaporation method on glass substrate maintained at room temperature. The properties of thin films are known to depend on their thickness, structure, defects, etc. Hence, we have investigated the properties of our samples as a function of various parameters. The characterization of the films shows that the structural and morphological properties are strongly related to the film thickness. However, the film’s photosensitivity reveals a different story.

2 Experimental

Thin SnS films of varying thicknesses were grown at rates greater than 2 nm s⁻¹ on microscopy glass substrate maintained at room temperature by thermal evaporation of SnS pellets at vacuums better than ≈4 × 10⁻⁵ Torr using a Hind High Vac (12A4D) coating unit. Different thicknesses were obtained by varying the deposition time. The starting material was SnS powder of 99.99% purity was provided by Himedia (Mumbai). The thicknesses of the films were measured using a Dektak surface profiler (150) that essentially consists of a stylus connected to a piezoelectric crystal. As the stylus moves across the film edge the mechanical pressure change on the crystal is converted to an electric signal that is displayed as film thickness by the computer interface. A Bruker D8 X-ray Diffractometer with a copper target (CuKα radiation, λ ~ 1.5406 Å) was used...
to determine the structure/crystallinity of the samples. The surface morphology of the samples was compared using a field-emission scanning electron microscope (FE-SEM, FEI-Quanta 200F) at an accelerating voltage of 10 kV. The hot-spot probe method was used to determine the conductivity type of the films, which without exception showed that the as-grown films were p-type in nature. The photoconductivity experiments were carried out at room temperature using a source meter SMU-01 of Marine (India). A tungsten lamp was used as the light source. Contacts were made using silver paste, which is known to give good ohmic contacts with SnS [25, 26]. A bias voltage was selected by making sure that the films did not crack or curl upon biasing. Also, observations were made on the film’s properties like conductivity/resistance to check whether they remained identical even after multiple cycles of measurements (i.e., whether results were reproducible and did not alter due to biasing). Based on these checks, a 10 V bias voltage was selected for the photo-current decay (PCD) measurements reported. Also, Jiang et al. have used the same bias voltage for SnS films of similar thicknesses [23].

3 Results and discussion

3.1 Structural and morphological analysis

Figure 1 shows the X-ray diffractograms of various samples whose thickness lie between 450 and 1680 nm. All the peak positions matched with those listed in ASTM Card No 79-2193 for SnS, having orthorhombic structure with lattice constants $a \approx 5.673$ Å, $b \approx 5.75$ Å, and $c \approx 11.76$ Å. As can be seen from the X-ray diffractograms there is a change in orientation with increasing film thickness. The texture coefficient was estimated to determine the preferred orientation of crystallites in the as-deposited films using the formula

$$T_{hkl} = \frac{\left( \frac{I_{hkl}}{I_{o(hkl)}} \right)}{\frac{1}{N} \sum_{i} \left( \frac{I_{hkl}}{I_{o(hkl)}} \right)}$$

where $T_{hkl}$ is the texture coefficient of the $(hkl)$ plane. This is evaluated using the intensity of the $(hkl)$ plane $(I_{hkl})$ obtained experimentally from the X-ray diffractograms, while $I_{o(hkl)}$ is the intensity listed in the ASTM Card for the corresponding $(hkl)$ peak and $N$ is the total number of diffraction peaks obtained in X-ray diffraction. Preferential orientation $(hkl)$ plane would have a large texture coefficient compared to the other planes. We obtained $T_{005} \approx 2.5$, $T_{113} \approx 1.5$, and $T_{200} \approx 1.8$ for 450 nm, 650–1160 nm, and 1580–1680 nm films, respectively, showing a shift from (005) orientation to (113) and then to (200) as the film thickness increases. The Miller indices suggest that the film’s orientation moves from $ab$ planes parallel to the substrate (i.e., $c$ or the long axis perpendicular to the substrate) to an orientation where the $ab$ planes are perpendicular to the substrate (long/$c$ axis parallel to the substrate). The three concerned planes are shown in Fig. 2. A change in orientation with film thickness was also observed by Sinsermsuksakul et al. [27] and explained as the grain’s attempt to minimize the surface energy.

It was observed that the X-ray diffraction peaks were displaced from their reported ASTM Card positions, indicative of residual strains (or residual stress, which is the product of strain and the elastic constant of the material) acting on the SnS unit cells. The strain along the perpendicular direction of the plane contributing to specular diffraction can be estimated using

$$\delta_{hkl} = \frac{d_{\text{exp}} - d_{\text{ASTM}}}{d_{\text{ASTM}}}$$

where $d_{\text{exp}}$ is the experimentally obtained inter-planar distance and $d_{\text{ASTM}}$ is that of a single crystal. The study of strain
with film thickness shows an interesting trend (Fig. 3, the line in the figure is for visual aid only) with films exhibiting both tensile and compressive strain. Whereas films with thickness less than or equal to 1160 nm exhibit tensile strain (i.e., $d_{\text{exp}} > d_{\text{ASTM}}$), those with thickness greater than 1160 nm exhibit compressive strain (i.e., $d_{\text{exp}} < d_{\text{ASTM}}$). Though the data points of Fig. 3 are scattered, the error bars suggest that the tensile and compressive strains acting is constant. Our texture coefficient calculation shows films with thicknesses between 450 and 1160 nm shifting from (005) to (113) orientation, however, Fig. 2 shows that the (113) orientation occurs when the $ab$ plane moves from parallel-to-substrate to a suspended one (with an angle of $\approx 44^\circ$ toward the substrate). Considering that only 450 nm films seem to have (005) orientation, hence, we can consider that the full range of thicknesses has just two orientations—resulting in tensile strain for one orientation, i.e., (113), and compressive strain for the second, (200). We shall investigate this further in our grain-size and film-morphology analyses.

The SEM micrographs (Fig. 4) show two different morphologies, where thinner films showed spherical grains and thicker films exhibited “needle”-shaped morphology. Correlating our SEM results with that of orientation and strain analysis (from XRD), we feel the change in morphology is due to the change in orientation, which is also the cause of variation in strain (from tensile to compressive). The needle-shaped morphology [28, 31] is typical when the $c$ or long axis is parallel to the substrate, thus confirming our assertion made while interpreting our X-ray diffraction results.

The average grain size of the SnS samples were determined from the XRD peaks according to the Scherrer formula [32]

$$D = \frac{0.9\lambda}{\text{FWHM} \cos \theta}, \quad (2)$$

where $D$ is the average grain size, $\lambda$ is the wavelength of the X-ray used ($\lambda = 1.5406 \, \text{Å}$), FWHM is the full width at half maximum intensity of the diffraction peaks and $\theta$ is the Bragg angle. Figure 5 shows the variation of average grain size with film thickness. Notice that the grain size of the sample with 450 nm film thickness, having a (005) orientation, does not follow the trend of samples with film thickness less than 1160 nm. This may be due to the differences in their ori-
entations. Initially, the average grain size increases with the thickness, however, on reaching a maximum value it shows a decreasing trend with the film thickness. Considering that the grains are not spherical for films with thicknesses greater than 1160 nm (Fig. 4), the grain size calculations based on Eq. (2) is indicative at best.

Again, as stated earlier, the results of Figs. 4 and 5 concur with that of Fig. 3 and suggest we are dealing with two orientations, for thin samples (thickness < 1160 nm) with c axis perpendicular or near perpendicular to the substrate (113) – and for thicker samples (thickness > 1160 nm) c parallel to the substrate (200). To summarize the analyses above, we have found the film orientation, morphology and strain are constant for thicknesses below and above 1160 nm, while the grain size varies systematically with film thickness. This would suggest that the lattice parameters (a, b, c) remain constant with film thickness, but take two different set of values, one below and one above film thickness of 1160 nm. The variation in grain size, hence, is due to the variation in ordering. This is mathematically expressed by the variation in u, v, w of the translation vector, given as

\[ \mathbf{T} = ua + vb + wc. \]

We now proceed to study the samples photoconductivity and thereafter investigate whether the orientation/strain or grain size contributes to the observations made.

### 3.2 Photoconductivity

To study the photoconductivity of the films, the I–V characteristics of the samples were measured with them exposed under a tungsten bulb. Interestingly, the resistivities of the thicker films (d ≥ 1160 nm) were found to be very high (≫10^8 MΩ, beyond the measuring capability of the instrument). A similar observation was made by Wang et al. [4]. Considering that there is a sudden change in resistivity as the film thickness is increased beyond 1160 nm, we believe this exceptionally high resistivity is related to the grain orientation (as seen in our structural analysis, thicker samples have c axis parallel to the substrate). Sinsermsuksakul et al. [27] have shown that the mobility of charge carriers is significantly lower along the direction of Van der Waals forces (which act along the c/long axis). Hence, with electrodes made on the film’s surface, we can appreciate the high resistance in thick SnS samples.

“Sensitivity” (S) is usually used as a figure of merit while discussing the photoconductivity of films and is given as [33, 36]

\[ S = \left( \frac{\sigma_L - \sigma_D}{\sigma_D} \right). \]

\(\sigma_L\) and \(\sigma_D\) are the film’s conductivity measured when exposed to light (L) and in the dark (D), respectively. Sensitivity, hence is a measure of how much conduction increases in a sample with light intensity. The increase in conductivity may be due to an increase in charge carriers [37, 38] or due to a change in mobility [39]. In polycrystalline or nanocrystalline samples, charge accumulation takes place at the grain boundaries, which manifests as a barrier potential. On illumination, some charge carriers are generated, part of which would recombine with the respective opposite charges, thereby reducing the barrier potential at grain boundaries. This reduction in turn would lead to an easy carrier movement across the boundaries and hence an increase in the charge carrier’s mobility. This phenomenon is called grain-boundary modulation [35]. The photoconductivity is given as [36]

\[ \Delta \sigma = q(\Delta p)\mu + q p(\Delta \mu), \]

where \(p\) is the charge carrier concentration (here restricted to holes considering that p-type material is under discussion) and \(q\) the charge associated with a single charge carrier, while \(\mu\) is the carrier mobility. Figure 6 shows the variation of sensitivity with intensity for four different thicknesses (less than 1160 nm) of nanocrystalline samples whose grain sizes were different. As can be seen, all the experimental data irrespective of the grain size follows the same trend. This would suggest that the sensitivity of p-SnS is independent of grain size and hence grain boundary, thus ruling out barrier modulation. Thus, any increase in conductivity is due to an increase in photoconductors or carriers created by illumination only. The above equation reduces to

\[ \Delta \sigma = q(\Delta p)\mu. \]

Figure 6 is also indicative of the fact that sensitivity is dependent on the illumination intensity. In fact, it is functionally given as [40, 22]

\[ S \propto I^\gamma, \]

where \(I\) represents the illumination intensity. The exponential factor \(\gamma\) can be evaluated from the slope of the straight
line obtained when Fig. 6 is plotted on a logarithmic scale. For our data we obtain $\gamma = 0.876$, which was found to be constant for all the thicknesses (450–960 nm). $\gamma < 1$ indicates the existence of traps within the bandgap and also the presence of recombination [35, 41]. Considering the grain size varied with film thickness and only the tensile strain remained constant, we suggest that the exponent factor $\gamma$ and in turn the photosensitivity depends on the film tensile strain. The tensile strain arises due to changes in the lattice parameter, which might be contributing to the appearance of energy levels in the bandgap. In fact, it is established that p-SnS contains Sn vacancies, which results in the introduction of acceptor levels within the bandgap [28, 42]. These acceptor levels in turn act as traps [43, 44] that contribute to persistent photocurrents (PPC).

Table 1 Decay time constants of various films obtained by curve fitting of the photocurrent data to Eq. (7).

| thickness (nm) | $\tau$ (s) |
|---------------|------------|
| 450           | 234.65     |
| 650           | 207.47     |
| 870           | 133.24     |
| 960           | 90.30      |

The vertical rise and drop in current upon switching illumination ON and OFF, respectively, is a result of charge carriers crossing the bandgap with no contribution of traps, whereas, the exponential rise and decay is the trap-assisted photocurrent. The trap-assisted photocurrent or the persistent photoconductivity (PPC) is dominant in thinner samples as compared to the thicker samples, as is evident by the larger vertical change regions of the PCD curve for samples with thickness $\geq 870$ nm. The persistent current is given by the equation [45, 43]

$$I(t) = I_0 + A_o \exp \left[ -\left( \frac{t}{\tau} \right)^{\beta} \right]. \quad (7)$$

where $\tau$ the decay-time constant and $\beta$ represents the stretching exponent constant. The $\tau$ values obtained by fitting an extended exponential function (Eq. (7)). For $\beta < 1$, the extended exponential function gives an exponential fit (Fig. 7A) marking the existence of single trap level within the bandgap [46]. For Fig. 7B, the fit was done on data points after the rapid fall terminated, based on visual examination of the trend in data. The decays for these samples were nonexponential with $\beta > 1$ indicative of a multiple/continuous distribution of defect states within the bandgap [47, 48]. The decay-time constants obtained for various samples are listed in Table 1. The large decay time constant indicates existence of trap centers within the forbidden bandgap of the film [23]. These trap centers increases the carrier lifetime [49] in the as-grown p-SnS thin films especially in the case of exponential PCD. We find the charge-carrier lifetime systematically decreases as film thickness increases. Considering an increased lifetime implies a reduced recombination rate allowing more time for the carriers to move without recombination, the material with long carrier lifetime and good sensitivity would be a useful material for photovoltaics [24]. In fact, to increase the efficiency of the solar cells one needs to increase the photosensitive layer’s absorption and the collection efficiency of the cell. The presence of traps in the material hinders the movement of charge carriers, thus decreasing their effective mobility, however, the carrier lifetime increases. In other words, the carrier mobility and lifetime product plays an important role in deciding the solar cell’s collection efficiency. A large carrier mobility–lifetime product ensures higher efficiencies [50]. Thus, the reduction in mobility can be compensated by an increase in carrier lifetime resulting in an optimum carrier mobility–lifetime product [24]. However, if the trap densities are very high, it would be counterproductive leading to degradation in solar-cell performance [51].

4 Conclusions Tin sulfide (SnS) thin films were fabricated by thermal evaporation on glass substrates maintained at room temperature. The films were found to be nanocrystalline with layered structure having either having (113) or (200) orientation. The orientation was found to have an effect on the film’s morphology and its properties, such as electrical conductivity. The poor conductivity of thicker films
caused by the $c$ axis being parallel to the substrate made it impossible to study the photoconductivity of these samples. However, thinner samples showed good photosensitivity and we observed persistent photocconductivity in them. This indicates the existence of traps within the forbidden energy gap of thin samples. The charge carrier’s lifetime was found to decrease with increasing film thickness, possibly due to the introduction of a multiple/continuous distribution of defect states within the bandgap with increasing film thickness. This would imply an improved photovoltaic performance in very thin samples of SnS with charge carriers reaching their respective electrodes without recombination. Also, we suggest the exponent factor ($\gamma$) and hence the photosensitivity depends on the position of the defect energy level, which manifests due to the tensile strain acting along the (113) direction.

Acknowledgements One of the authors (Y.G.) would like to express her gratitude to DST (India) for the financial assistance in terms of fellowship under the INSPIRE program (Fellowship No. IF131164).

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