Antimony-Doped Tin(II) Sulfide Thin Films

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ABSTRACT: Thin-film solar cells made from earth-abundant, inexpensive, and nontoxic materials are needed to replace the current technologies whose widespread use is limited by their use of scarce, costly, and toxic elements.1 Sn monosulfide (SnS) is a promising candidate for making absorber layers in scalable, inexpensive, and nontoxic solar cells. SnS has always been observed to be a p-type semiconductor. Doping SnS to form an n-type semiconductor would permit the construction of solar cells with p-n homojunctions. This paper reports doping SnS films with antimony, a potential n-type dopant. Small amounts of antimony (~1%) were found to greatly increase the electrical resistance of the SnS. The resulting intrinsic SnS(Sb) films could be used for the insulating layer in a p-i-n design for solar cells. Higher concentrations (~5%) of antimony did not convert the SnS(Sb) to low-resistivity n-type conductivity, but instead the films retain such a high resistance that the conductivity type could not be determined. Extended X-ray absorption fine structure analysis reveals that the highly doped films contain precipitates of a secondary phase that has chemical bonds characteristic of metallic antimony, rather than the antimony–sulfur bonds found in films with lower concentrations of antimony.

KEYWORDS: thin films, doping, semiconductor, tin sulfide, antimony

INTRODUCTION

In the past few decades, tin(II) sulfide (SnS) has gained much attention as a possible alternative absorber material for the next generation of thin-film solar cells to replace the current best-developed technology based on Cu(In,Ga)Se2 and CdTe, which involve toxic Cd and rare elements In, Ga, and Te. In addition to low toxicity, low cost, and natural abundance of its constituent elements, SnS has high optical absorption (α > 104 cm−1) above the direct absorption edge at 1.3–1.5 eV.2,3 It has native p-type conduction because of the small enthalpy of formation of tin vacancies, which generate shallow acceptors.4 SnS-based heterojunction solar cells have been reported using different n-type partners such as ZnO,5 CdS,6 Cd1−xZnxS,5 SnS2,8 TiO2,6 and a-Si.10 The power conversion efficiencies (η) achieved so far on these planar heterojunction devices are still small (~1%) were found to greatly increase the electrical resistance of the SnS. The resulting intrinsic SnS(Sb) films could be used for the insulating layer in a p-i-n design for solar cells. Higher concentrations (~5%) of antimony did not convert the SnS(Sb) to low-resistivity n-type conductivity, but instead the films retain such a high resistance that the conductivity type could not be determined. Extended X-ray absorption fine structure analysis reveals that the highly doped films contain precipitates of a secondary phase that has chemical bonds characteristic of metallic antimony, rather than the antimony–sulfur bonds found in films with lower concentrations of antimony.

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EXPERIMENTAL SECTION

Sb-Doped SnS Thin Film. Pure, stoichiometric, single-phase SnS thin films can be obtained by atomic layer deposition (ALD) from the reaction of bis(N,N′-disopropylacetamidinato)tin(II) [Sn(MeC(N-Pro)2, referred here as Sn(amd)2] and hydrogen sulfide (H2S). Rather than using ALD as previously reported, SnS thin films were deposited using a modified chemical vapor deposition (CVD) process, referred here as a pulsed-CVD, to speed up the deposit rate to ~15 times higher than that of ALD. The sequence of one cycle of a pulsed-CVD is composed of (i) injection of Sn(amd)2 vapor using N2 assistance, (ii) injection of H2S gas to mix and react with the Sn(amd)2 vapor trapped inside the deposition zone, and (iii) evacuation of the gas mixture and byproducts. Unlike conventional ALD, there is no purging of excess Sn(amd)2, before H2S injection, thereby increasing the deposition rate at the cost of some nonuniformity in the film thickness along the length of the reactor. The substrate temperature was set to 200 °C. The tin precursor source was kept at 95 °C. A gas mixture of 4% H2S in N2 (Airgas Inc.) was used as the source of sulfur. H2S is a toxic, corrosive, and flammable gas (lower flammable limit of 4%).18 Thus, it should be handled with caution. An appropriate reactor design for H2S compatibility can be found elsewhere.17 The partial pressures of Sn(amd)2 and H2S after injecting into the deposition zone for each pulsed-CVD cycle are approximately 100 mTorr and 240 mTorr, respectively.

SnS thin films can be prepared from ALD using the reaction of tris(dimethylamido)antimony(III) [Sb(NMe2)3] (Sigma-Aldrich) and hydrogen sulfide.20 The stop-flow ALD mode15,21 was used for the deposition. The antimony source was kept at room temperature (25 °C). The total exposure of Sb(NMe2)3 and H2S for each of an ALD cycle were approximately 0.7 and 1.1 Torr·s, respectively. Sb-doped SnS thin films were deposited by inserting cycles of ALD Sb2S3 into the deposition of SnS. By varying the ratio between the numbers of Sb2S3 and SnS cycles, controlled concentrations of Sb++ in SnS can be obtained. For example, a 1% cycle ratio film, SnS(1% Sb), was prepared by alternating between 99 cycles of SnS and 1 cycle of Sb2S3. Three samples were deposited using 1%, 2%, and 5% Sb cycles to determine the effect of Sb concentration on the crystal structure and electrical properties of the films.

Material Characterization. Film morphology was characterized using field-emission scanning electron microscopy (FESEM, Zeiss, Ultra-55). The film thickness was determined from cross-sectional SEM. The elemental composition of the films was determined by Rutherford backscattering spectroscopy (RBS, Ionex 1.7 MV Tandetron) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). X-ray photoelectron spectroscopy (XPS, Surface Science, SSX-100) was used to detect possible carbon, nitrogen, and oxygen contamination in the films. The crystal structures of SnS and Sb-doped SnS thin films were examined by X-ray diffraction (XRD, PANalytical X’Pert Pro) with Cu Kα radiation (λ = 1.542 Å) using a 2θ/θ scan. The lattice parameters were calculated from least-squares fitting to the position of the Bragg peaks determined by Gaussian fit. Electrical properties of the films were characterized by Hall measurement (MMR technologies K2500) using the Van der Pauw method at 300 K. Synchrotron-based X-ray absorption fine structure (EXAFS) was used to study the local atomic environment of the antimony dopant. Synchrotron measurements were conducted at beamline 20-BM at the Advanced Photon Source of Argonne National Laboratory.23

RESULTS AND DISCUSSION

The obtained SnS and Sb-doped SnS films appeared smooth, pinhole free, and adhere well to the substrate (α-SiO2). Figure 1 shows the surface morphology of an undoped SnS film and a SnS(5% Sb) film grown by pulsed-CVD at 200 °C, as observed by SEM. Because of the low level of doping, the surface
morphology of undoped SnS and all of the Sb-doped SnS samples are not significantly different. The film thicknesses of all the samples are approximately 500 nm, as determined from cross-sectional SEM. The chemical composition of the undoped SnS film was measured using RBS to be stoichiometric SnS to within the detection limit (±1%). As in ALD SnS20 and ALD Sb2S3,20 XPS does not detect any carbon or nitrogen contamination in the Sb-doped SnS films deposited at this particular temperature.

The atomic concentration of Sb in SnS was estimated by ToF-SIMS (Figure 2a) from the average intensity of Sb and Sn++ using a Cs+ sputter source. If the efficiencies of generating Sb and Sn++ ions are assumed to be the same, then the Sb concentrations in SnS(1% Sb), SnS(2% Sb), and SnS(5% Sb) are determined to be 0.7 ± 0.2%, 1.2 ± 0.3%, and 4.5 ± 0.3%, respectively. Because we lack absolute concentration standards for SIMS analysis of dilute Sb in Sn, these concentrations could be in error by a constant calibration factor. Because of the chemical similarity of tin and antimony metals, it is expected that the calibration factor should not deviate significantly from unity.

From Figure 2b, a slight deviation from linearity between the Sb concentration and Sb growth cycle percentage was observed in the SnS(5% Sb) sample. If the reactivity of Sb(III) precursor and H2S was identical on SnS and SnS(5% Sb) surfaces, then the atomic concentrations of Sb would be linearly proportional to their respective cycle percentages. However, the reactivities and chemisorptions on different surfaces, in general, are not the same. Thus, the actual Sb concentrations may not be exactly proportional to the cycle ratios, as observed in this case. This
phenomenon was also observed in other doping systems, such as Al doped into ZnO, TiO₂, and SnO₂.

Figure 3a shows the X-ray diffraction (XRD) patterns of SnS and Sb-doped SnS films, which correspond to the orthorhombic structure of Herzenbergite SnS (PDF No. 00-039-0354, a = 4.3291 Å, b = 11.1923 Å, c = 3.9838 Å). Other impurity phases (i.e., Sn₂S₃ and SnS₂) were not detected in the deposited films. At 4.5% Sb-concentration, one Bragg peak at 2θ = 28.7° was observed, but this peak does not belong to the known SnS or Sb₂S₃ phases. The peak could be assigned to the (040) plane of Valentinite Sb₂O₃ (PDF No. 01-072-2738) or the (012) plane of rhombohedral Sb (PDF No. 00-035-0732). However, depth profiling XPS reveals no oxygen contamination in this sample. Thus, this Bragg peak is most likely due to Sb; presumably, the concentration of Sb in this sample exceeded the solid solubility at deposition temperature (or upon cooling); the resulting supersaturation was relieved via precipitation of a secondary phase. Figure 3b presents the XRD in the region near the (111) lattice plane. Since the Bragg angle θ is inversely proportional to the lattice spacing d, which for the (111) plane equals to \[ d = \frac{\lambda}{2\sin \theta} \] where \( \lambda \), a, b, and c are lattice constants, the shift of the (111) peak position to the higher θ value indicates the crystal lattice shrinkage after Sb-doping. This unit cell volume decreases with increasing Sb concentration from 0.7% to 1.2% probably because of substitution of smaller Sb³⁺ for Sn²⁺, but increases less with higher (4.5%) doping because of the precipitation of the secondary phase, as we shall see by correlating these results with EXAFS.

Table 1 shows some electrical properties of SnS and Sb-doped SnS thin films at 300 K. The undoped SnS thin film shows resistivity of 175 Ω cm, hole concentration of 4.4 × 10¹⁵ cm⁻³, and mobility of 8 cm² V⁻¹ s⁻¹. The addition of small amounts of Sb, even at 0.7% concentration, effectively produces an insulating film with resistivity increased to 3.82 × 10⁴ Ω cm, more than 2 orders of magnitude higher than the undoped film. Upon increasing Sb concentration up to 1.2%, the resistivity of Sb-doped SnS film remains roughly the same, 3.74 × 10⁴ Ω cm. However, the film resistivity drops by half to 1.60 × 10⁴ Ω cm when the Sb concentration increases up to 4.5%. Unfortunately, the carrier concentration and conductivity type of the Sb-doped SnS films cannot be measured from the current Hall setup because of their high resistivities.

To clarify the mechanism behind the anomalous rise and fall of SnS film resistivity with increasing Sb doping concentration, we performed Extended X-ray Absorption Fine Structure (EXAFS) measurements at the Sb edge. The EXAFS technique is sensitive to the local atomic environment surrounding the dopant atoms, elucidating the chemical state of the dopant atoms (e.g., substitutional, interstitial, or second-phase particle). EXAFS was performed at the Sb K-edge X-ray absorption edge on the 1.2% SnS(Sb) film, the 4.5% SnS(Sb) film, the Sn₂S₃ film, and an Sb metal reference standard. We also performed EXAFS on the 0.7% SnS(Sb) film, but the signal was too weak to obtain a high-quality EXAFS spectrum. Data were analyzed using...
Table 1. Summary of Sb Concentrations, Lattice Constants, and Electrical Properties of Undoped and Sb-Doped SnS Films

<table>
<thead>
<tr>
<th>sample</th>
<th>cycle ratio</th>
<th>Sn:Sb</th>
<th>%Sb in SnS</th>
<th>lattice constant (Å)</th>
<th>resistivity (Ω cm)</th>
<th>carrier density (cm⁻³)</th>
<th>mobility (cm²/(V s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnS</td>
<td>1:0</td>
<td>0</td>
<td>0.00 ± 0.11</td>
<td>11.19 ± 0.02</td>
<td>3.99 ± 0.01</td>
<td>175</td>
<td>+4.4 × 10¹⁵</td>
</tr>
<tr>
<td>SnS(1% Sb)</td>
<td>99:1</td>
<td>0.1</td>
<td>0.6 ± 0.11</td>
<td>11.19 ± 0.02</td>
<td>3.99 ± 0.01</td>
<td>175</td>
<td>+3.82 × 10¹⁰</td>
</tr>
<tr>
<td>SnS(2% Sb)</td>
<td>49:1</td>
<td>1.2</td>
<td>1.2 ± 0.13</td>
<td>11.17 ± 0.02</td>
<td>3.99 ± 0.01</td>
<td>175</td>
<td>+3.74 × 10¹⁰</td>
</tr>
<tr>
<td>SnS(5% Sb)</td>
<td>19:1</td>
<td>4.5</td>
<td>4.5 ± 0.13</td>
<td>11.19 ± 0.02</td>
<td>3.99 ± 0.01</td>
<td>175</td>
<td>+1.60 × 10¹⁰</td>
</tr>
</tbody>
</table>

Figure 4. Summary of EXAFS measurements: The magnitude of the complex Fourier transform of χ(k) at the Sb edge of the 1.2% SnS(Sb) film, 4.5% SnS(Sb) film, Sb₂S₃ film, and Sb metal standard. The peak at 2 Å in the Sb₁S₁ data is due to sulfur nearest-neighbors of antimony.

Table 2. Path Names for Each Structure Model with Corresponding Half-Path Lengths and Coordination Numbers

<table>
<thead>
<tr>
<th>structure model</th>
<th>path</th>
<th>Rᵥᵣ (Å)</th>
<th>N</th>
<th>Sn(Sb) (a)</th>
<th>path</th>
<th>Rᵥᵣ (Å)</th>
<th>N</th>
<th>Sb₂ (b)</th>
<th>path</th>
<th>Rᵥᵣ (Å)</th>
<th>N</th>
<th>Sb metal (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnS(Sb₁)</td>
<td>S₁</td>
<td>2.6237</td>
<td>1</td>
<td>[Sb₁] − S₁</td>
<td>S₂</td>
<td>2.6658</td>
<td>2</td>
<td>[Sb₂] − S₂</td>
<td>S₃</td>
<td>2.9063</td>
<td>3</td>
<td>Sb₁</td>
</tr>
<tr>
<td>Sn(Sb₂)</td>
<td>S₁</td>
<td>3.2908</td>
<td>2</td>
<td>[Sb₂] − S₁</td>
<td>S₂</td>
<td>3.3908</td>
<td>1</td>
<td>[Sb₂] − S₂</td>
<td>S₃</td>
<td>3.4937</td>
<td>2</td>
<td>Sb₂</td>
</tr>
<tr>
<td>Sn(Sb₃)</td>
<td>S₁</td>
<td>3.9870</td>
<td>2</td>
<td>[Sb₃] − S₁</td>
<td>S₂</td>
<td>3.9048</td>
<td>1</td>
<td>[Sb₃] − S₂</td>
<td>S₃</td>
<td>3.9780</td>
<td>2</td>
<td>Sb₂</td>
</tr>
</tbody>
</table>

All paths are single-scattering events with Sb as the atom of origin. For model (b), the atom of origin is shown in brackets to distinguish between the two distinct lattice sites of Sb in SnS(Sb), the trivalent Sb₁ and quintivalent Sb₂. Nearest-neighbor distances are given in Table 2.

Figure 5. Ball-and-stick representation of (a) SnS with the SbSn substitution at the central atom, (b) Sb₂Sn, and (c) Sb metal. Green: Sn; Blue: S; Red: Sb. For clarity, the cluster sizes shown are smaller than those used for EXAFS fitting. Note the two distinct lattice sites of Sb in Sb₂Sn, the trivalent Sb₁ and quintivalent Sb₂. Nearest-neighbor distances are given in Table 2.

Figure 6 shows these EXAFS data and fits, and Figure 7 shows the real parts and magnitudes of the Fourier transform of these data. Table 3 gives the best-fit values of parameters for the fitted spectra. Attempts to refine model (c) for the 1.2% SnS(Sb) data or models (a) and (b) for the 4.5% SnS(Sb) data were not possible with R values under 60%. The Sn substitutional [SnS(Sb₃)] model qualitatively gives the best fit for the 1.2% SnS(Sb) data, closely matching the phase and amplitude of χ(R) beyond the sulfur shells. Although the SnS(Sb) model also fits reasonably well to the data, formation of the SnS(Sb) phase is unsupported by XRD of the 1.2% SnS(Sb) film. Peaks corresponding to SnS(Sb) were not observed in the XRD pattern, and the SnS lattice constant shift indicates an incorporation of Sn into the SnS lattice. Furthermore, the phase composition of the SnS-Sb system as observed in the XRD pattern, and the SnS lattice constant shift indicate an incorporation of Sn into the SnS lattice.
The possibility that a small fraction of Sb exists in the Sb$_2$S$_3$ phase, falling below the sensitivity of XRD. The Sb metal model matches well with the 4.5% SnS(Sb) EXAFS data. This supports our hypothesis that the antimony in the 4.5% SnS(Sb) is present predominantly in a secondary phase, consistent both with our XRD observation of a new peak emerging with high doping density, and with the aforementioned phase composition study of the SnS-Sb system. The formation of Sb metal observed by EXAFS may underlie the decrease of resistivity at the highest Sb doping level; since the majority of dopant atoms in this film do not occupy substitutional lattice sites, the degree of compensation is reduced, and the free hole concentration is increased. We also note that dopant precipitation into metallic nanoparticles has been observed for other systems such as metal-doped ZnO.

**CONCLUSION**

In conclusion, Sb-doped SbS thin films were deposited by pulsed-CVD using the reaction of Sn(MeC(N-iPr)$_2$)$_2$ and Sn(NMe$_2$)$_3$ with H$_2$S. Small amounts of Sb (~1%) in SnS increase the film resistivity by more than 2 orders of magnitude, most likely due to substitutional doping. Sb addition at low levels is an effective means of producing compensated, insulating SnS films, which could be useful in solar cells with a p-i-n heterostructure. The conductivity type of the Sb-doped SnS films could not be determined because of their high resistivity. Increasing the doping level from 1.2% to 4.5% appears to cause clustering of the Sb into metallic precipitates.
Table 3. Best-Fit EXAFS Parameters and Corresponding Paths for Three Structure Models

<table>
<thead>
<tr>
<th>parameters</th>
<th>SnS(Sb)</th>
<th>SbS</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_r$</td>
<td>10.2 (2.7)</td>
<td>10.6 (1.0)</td>
<td>9.9 (2.3)</td>
</tr>
<tr>
<td>$\delta_1$</td>
<td>0.82 (0.05)</td>
<td>0.93 (0.10)</td>
<td>0.77 (0.25)</td>
</tr>
<tr>
<td>$\delta_R$</td>
<td>-0.15 (0.02)</td>
<td>0.02 (2.47)</td>
<td>0.0069 (0.017)</td>
</tr>
<tr>
<td>$\delta_0$</td>
<td>0.050 (0.089)</td>
<td>-0.01 (0.07)</td>
<td>0.0032 (0.060)</td>
</tr>
<tr>
<td>$\delta_r$</td>
<td>0.21 (0.35)</td>
<td>-0.16 (0.36)</td>
<td></td>
</tr>
<tr>
<td>$\delta_ar$</td>
<td>-0.08 (0.11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta_ar$</td>
<td>-0.26 (0.13)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_1^2$</td>
<td>0.0052 (0.0020)</td>
<td>0.003</td>
<td>0.0051 (0.0024)</td>
</tr>
<tr>
<td>$\sigma_2^2$</td>
<td>0.011 (0.022)</td>
<td>0.0063 (0.0072)</td>
<td>0.019 (0.011)</td>
</tr>
<tr>
<td>$\sigma_3^2$</td>
<td>0.014 (0.039)</td>
<td>0.0056 (0.0031)</td>
<td></td>
</tr>
<tr>
<td>$\sigma_4^2$</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*Models (a) and (b) are fit to 1.2% SnS(Sb) data, and model (c) is fit to 4.5% SnS(Sb) data. See Table 1 for path details.*

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**Notes**
The authors declare no competing financial interest.

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