Phase Engineering of 2D Tin Sulfides

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**1. Introduction**

Two-dimensional (2D) tin sulfides belong to a broad class of van-der-Waal (vdW) materials that have been the subject of intense research. Their constituent elements tin (Sn) and sulfur (S) are inexpensive and abundant in nature. The atomically thin geometry combined with the ability to tune the electronic structure of 2D tin sulfides as a function of thickness makes them attractive candidates to be used in nanoelectronics and optoelectronic devices.[1] These sulfides can crystallize in a variety of crystal phases, such as tin disulfide (SnS$_2$) and tin monosulfide (SnS), which possess distinct physical and electronic properties.[2] Therefore, identifying approaches for controlling crystal phase is essential for tailoring the properties of these materials to specific applications.

Tin sulfides possess desirable properties for numerous electronic and optical applications. SnS$_2$ is an intrinsic n-type layered semiconductor with a bandgap of 2.18–2.44 eV.[3–6]
Potential applications of SnS$_2$ include novel electronics devices, flexible electronics, optoelectronics, and energy storage.\cite{7-10} The high electron affinity of SnS$_2$ makes it a suitable candidate to achieve broken-gap heterostructures which enable the design and operation of 2D tunnel field-effect transistor (TFETs).\cite{7,11} Moreover, SnS$_2$ crystals show high charge carrier mobility ($\approx 230$ cm$^2$ (Vs)$^{-1}$) combined with high on/off current ratios ($>10^6$) in field-effect transistors (FETs), fast photocurrent response time ($=5$ µs) in photodetectors, and high theoretical specific capacity ($=920$ mAhg$^{-1}$) in lithium-ion batteries (LIBs) as the anode material.\cite{1,9,12} On the other hand, SnS is an intrinsically p-type layered semiconductor with an indirect and a direct bandgap at $\approx 1$–1.1 and $\approx 1.3$–1.5 eV, respectively.\cite{3,13-16} The desirable bandgap, high absorption coefficient ($>10^4$ cm$^{-1}$) and sensitivity of its properties to changes in dimensionality, and elemental composition make SnS a promising material for optoelectronic applications.\cite{15,17-21} Furthermore, combined SnS and SnS$_2$ heterostructures have been reported to show improved photocatalytic performance on photodegrading organic dyes, compared with that of as-synthesized pure phases of SnS and SnS$_2$.\cite{4}

Selective pure phase synthesis of single crystalline tin sulfides is a challenging task due to the high sensitivity of the different phases to growth conditions. Tin sulfides have been previously synthesized mostly in the form of bulk single crystals or thin films. The bulk single crystals have been grown by the Bridgman method\cite{22,23} and chemical vapor transport;\cite{2,24} the thin films have been synthesized using various deposition methods.\cite{5,25-27} However, relatively few studies have reported the synthesis of 2D crystals of SnS$_2$\cite{3,9,28} and SnS\cite{11,29} using vapor-phase methods.

In this study, we demonstrate phase-controlled synthesis of 2D SnS$_2$ and SnS crystals using an atmospheric pressure vapor-phase method. The fundamental structural and electronic properties of each crystal phase are comprehensively investigated using optical microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), Raman spectroscopy, and ultraviolet photoelectron spectroscopy (UPS) and compared with results of ab initio density functional theory (DFT) calculations.

2. Results and Discussion

2.1. Morphology and Atomic Structure

2D tin sulfide crystals with lateral sizes over tens of microns were synthesized by atmospheric pressure vapor-phase growth method in a horizontal quartz tube furnace as shown in Figure 1a. In a typical synthesis, SnO$_2$ and S powder precursors were located at the center and upstream of the tube furnace, respectively. SiO$_2$ substrates were placed close to each other at downstream of the tube furnace. The 2D crystals were obtained on the SiO$_2$ substrates by heating the tube furnace to $705°C$ and maintaining this temperature for 40 min before cooling down to room temperature (RT) (see Section 4 for details).

![Figure 1](https://example.com/image1.png)

**Figure 1.** a) The growth setup for the growth of SnS$_2$ and SnS crystals. Optical microscopy images of b) SnS$_2$ and c) SnS crystals grown on SiO$_2$ substrates. Low magnification ADF–STEM images of d) SnS$_2$ and e) SnS crystals transferred to a TEM grid. Filtered atomic-resolution ADF–STEM image of f) SnS$_2$ and g) SnS. Ball-and-stick models are overlapped to highlight atomic positions.
Optical images of the SiO$_2$ substrates show that SnS$_2$ crystals (Figure 1b) grow at a lower substrate temperature of $\approx$425 °C while SnS crystals (Figure 1c) form at a higher temperature of $\approx$550 °C. SnS$_2$ crystals show a trapezoidal shape, and SnS crystals have a rectangular shape.

Since SnS and SnS$_2$ possess different crystal structures, atomic resolution STEM imaging can be used to directly verify the phases obtained from the growth. SnS$_2$ and SnS crystals obtained by the previously described recipe were first transferred to separate TEM grids and imaged in a STEM (see Section 4 for details). Figure 1d,e show low magnification annular dark-field (ADF)–STEM images of SnS$_2$ and SnS crystals, respectively. Figure 1f,g show filtered high-resolution ADF–STEM images of both phases obtained along the [001] zone axis where the crystal structure of the two phases can be distinguished. The image filtering procedure followed that used by Wu et al.$^{[30]}$ SnS$_2$, as seen in the ADF–STEM image, appears to crystallize in the 1T polymorph. This arrangement, which can be clearly differentiated from the image of SnS$_2$.

2.2. Growth Mechanisms

The growth of the 2D crystals can be explained by the reaction of SnO$_2$ and S. When the temperature of the tube furnace is above the Tammann temperature of SnO$_2$ ($T_{\text{Tamm}} = \approx$400 °C$^{[33]}$), SnO$_2$ evaporation will be initiated, even though the applied temperature is lower than its melting point in powder form ($T_{\text{melt}} = 1350$ °C$^{[34]}$). At the early stage of the growth ($\approx$400 °C), SnO$_2$ vapor from solid SnO$_2$ powders makes contact with the substrate and forms small SnO$_2$ clusters which act as nucleation sites for tin sulfide crystals.$^{[35]}

SnO$_2$ vapor from solid SnO$_2$ powders reacts with S vapor to initiate the formation of SnS$_2$ according to (1)$^{[3]}$

$$\text{SnO}_2 (s) + 1.5\text{S}_2 (g) \rightarrow \text{SnS}_2 (s) + \text{SO}_2 (g) \quad (1)$$

As the reaction temperature increases, the growth of SnS$_2$ will eventually stop due to its phase instability at the high temperature.$^{[2,36,37]}$ At the same time, S source will be eventually depleted, which results in a reducing atmosphere in the tube. As a result, SnS growth will be favored according to (2)$^{[3]}

$$\text{SnO}_2 (s) + \text{S}_2 (g) \rightarrow \text{SnS} (s) + \text{SO}_2 (g) \quad (2)$$

To help further understand the underlying growth mechanisms of tin sulfide crystals, we performed a series of experiments by using three different growth recipes. Recipe I served as the control experiment where the quartz tube was heated from RT to 705 °C and then kept at this temperature for 40 min, followed by cooling down to RT. In recipe II, the furnace with the quartz tube was heated from RT to 625 °C, and immediately cooled down to RT without further heating. For recipe III, the quartz tube was initially held outside the furnace. While the furnace was being heated to 705 °C, the quartz tube was immediately slid inside the furnace at 625 °C. Then, the furnace with the quartz tube was kept at 705 °C for 40 min, followed by cooling down to RT. Only one long rectangular SiO$_2$ substrate was used for each experiment, and the growth parameters such as heating rate, gas flow rate, pressure, precursors, and substrates were kept constant for all the experiments.

Recipe I yielded both SnS$_2$ and SnS crystals, but the two were spatially separated on the substrate as shown in Figure 2a. SEM imaging (Figure 2b,c) and Raman spectroscopy (see Section 2.3) confirmed that SnS was grown on the hotter side of the substrate compared to SnS$_2$. On the other hand, recipe II resulted in primarily SnS$_2$ crystals at the lower temperature side of the substrate while recipe III gave mainly SnS crystals, which appears only in the hotter region. These results indicate that the growth of SnS$_2$ crystals is initiated mostly during the early stage of heating, while the formation of SnS crystals starts in the later stage of the heating. Hence, the formation of SnS occurs at higher temperatures compared to that of SnS$_2$, which is consistent with results of previous reports on the growth of SnS$_2$ and SnS crystals.$^{[32,36,37]}

We also studied the trace reaction products of SnO$_2$ (Figure 2d) and S found in the SnO$_2$ crucible. It was found that recipe II produced yellow transparent SnS$_2$ powders (Figure 2e), while recipes I and II yielded dark grey SnS powders (Figure 2f) as confirmed by Raman spectroscopy (see Section 2.3). For recipe II, since the growth was performed at low temperature for a short period of time, SnO$_2$ powders were sulfurized to form solid SnS$_2$ as a result of the reaction according to Equation (1). For recipes I and III, as the reaction proceeds, solid SnS$_2$ dissociation occurs as a result of the incongruent sublimation, which is promoted by both higher temperature and S depletion.$^{[30]}$ The dissociation of solid SnS$_2$ results in the phase transition from SnS$_2$ to SnS by (3)$^{[30]}

$$\text{SnS}_2 (s) \rightarrow \text{SnS} (s) + 0.5 \text{S}_2 (g) \quad (3)$$

In this series of experiments, we also observed a growth of multi-stacked SnS$_2$ crystals (Figure 2g–i). The interlayer S vdW interactions between consecutive SnS$_2$ layers can result in misorientation of the layers during growth. 2D multi-stacked SnS$_2$ crystals with varying configurations may possess some novel electronic and optical properties. Controlling stacking is beyond our scope in this study, but we point out that this simple method can be further optimized in order to achieve the control over the stacking.

2.3. Raman Spectra and Calculated Vibrational Frequencies

We performed Raman spectroscopy on the SnS$_2$ and SnS crystals obtained by the discussed growth recipes. The Raman spectra of an 8L SnS$_2$ crystal ($\approx$5.08 nm as measured in AFM with monolayer thickness of 0.6 nm$^{[11]}$) show a strong Raman peak at 314.9 cm$^{-1}$, corresponding to the $A_{1g}$ phonon mode$^{[19]}$ of SnS$_2$ (Figure 3a–c). In addition to the $A_{1g}$ mode, an intra-layer $E_{g}$ mode$^{[19]}$ with peak at $\approx$206.2 cm$^{-1}$ is observed in multilayer (ML) SnS$_2$ crystal with a thickness of $\approx$17.94 nm (30L) (Figure 3d–f). The absence of the
The Raman spectra from a ML SnS crystal (Figure 3g) was also measured. The thickness of the SnS crystal was estimated to approximately 30L (determined by cross-sectional STEM image in Figure 3h). The Raman spectra of the SnS crystal show a very different Raman pattern (Figure 3i) with the peaks centered within the range of 50–250 cm\(^{-1}\). The peaks at 95.6, 192.0, and 218.3 cm\(^{-1}\) can be assigned to the \(A_g\) mode, and the peak at 163.9 cm\(^{-1}\) corresponds to the \(B_{3g}\) phonon mode\[^{[3,40]}\] of SnS.

To support results of the experimental Raman spectroscopy, we calculated the zone-center vibrational modes of bulk SnS\(_2\) and SnS using ab initio DFT (see Section 4 for details). The vibrational modes at \(\Gamma\) point gave us insight into the allowed Raman active modes for each phase. For bulk SnS\(_2\), we calculated the vibrational modes that correspond to the out-of-plane \(A_{1g}\) and in-plane \(E_g\) Raman active modes. The calculated values of 313 and 204 cm\(^{-1}\) obtained for the \(A_{1g}\) and \(E_g\) modes, respectively, are in good agreement with the Raman spectrum we obtained for the 2D SnS\(_2\) crystal (Table 1).

For bulk SnS, we also calculated vibrational modes that correspond to the \(A_g\) and \(B_{3g}\) Raman active modes of the bulk orthorhombic structure of SnS. Based on the displacements of these modes, we determined \(A_g\) modes at 95, 196, and 216 cm\(^{-1}\) and the \(B_{3g}\) mode at 163 cm\(^{-1}\). These values are also in good agreement with our assignment of the Raman modes using the measured Raman spectra (Table 1) and prior Raman scattering studies on SnS\[^{[40]}\].

The agreement between our theoretical calculations of the Raman modes for each phase of tin sulfides and our experimental Raman spectra is further demonstration of the controlled growth we have over each phase. Moreover, we do not observe Raman peaks at 474, 632, or 774 cm\(^{-1}\) associated with SnO\(_2\).\[^{[41]}\] This implies negligible chemical reaction between the crystals and substrate.\[^{[35]}\]

2.4. Electronic Structure: Experiment and Calculation

The ionization potential for each tin sulfide phase can be determined by UPS. Using the helium (He) source at photon energies of 21.22 eV, we determined the ionization
potential, \( \phi \), by subtracting the width of the UPS spectra from 21.22 eV. We determined the ionization potential of our as grown SnS\(_2\) and SnS crystals and compared them to the measurements on commercial SnS\(_2\) crystals (2Dsemiconductors Inc.). The ionization potential of our as-grown SnS\(_2\) was found to be 7.51 eV (Figure 4a), close to that of commercial SnS\(_2\) crystal (7.7 eV) (Figure 4b). The ionization potential of SnS was determined to be 5.78 eV (Figure 4c).

Using DFT we evaluated the ionization potentials for SnS and SnS\(_2\) using an explicit slab model. 8L slabs of (001) SnS\(_2\) and (100) SnS were predicted to have bandgaps of 2.31 and 1.07 eV, respectively, which are close to the bandgap values for the respective bulk structures. Calculations of each 8L structure were then used to obtain the difference between the average of the electrostatic potential in the bulk and the eigenenergies with respect to the vacuum potential. This provided an ionization potential of 7.51 and 4.9 eV for SnS\(_2\) and SnS, respectively, which is in good agreement with the ionization potential of 7.51 and 5.78 eV we obtain for SnS\(_2\) and SnS, respectively.

3. Conclusion

Highly crystalline 2D SnS\(_2\) and SnS crystals with lateral sizes over tens of microns have been directly synthesized on SiO\(_2\).

Table 1. Comparison of experimentally measured and ab initio DFT calculated Raman spectra peak positions in SnS\(_2\) and SnS in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Phases</th>
<th>SnS(_2)</th>
<th>SnS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman modes</td>
<td>( A_{1g} )</td>
<td>( E_g )</td>
</tr>
<tr>
<td>Experimental</td>
<td>314.9</td>
<td>206.2</td>
</tr>
<tr>
<td>Calculated</td>
<td>313</td>
<td>204</td>
</tr>
</tbody>
</table>

Figure 4. UPS spectra acquired for a) our as-grown SnS\(_2\), b) commercial SnS\(_2\) crystal, and c) our as-grown SnS crystal.
substrates using a simple atmospheric pressure vapor-phase method. High-resolution ADF–STEM imaging reveals the phases of 2D hexagonal SnS$_2$ (1T) and orthorhombic SnS crystals. The phase purity of SnS$_2$ and SnS crystals is confirmed by the analysis of the Raman and UPS spectra, and the results are corroborated by ab initio DFT calculations. A series of growth experiments are performed to determine the growth process of the 2D crystals. It is found that temperature determines the phase of each crystal. SnS$_2$ crystals grow at lower temperatures compare to the case of SnS crystals. Moreover, we have showed that the hexagonal SnS$_2$ phase can be transformed into orthorhombic SnS phase upon high temperature treatment during growth. This temperature controlled process is advantageous for the purpose of avoiding highly toxic byproducts such as H$_2$S in H$_2$ reduction. Overall, these results are useful for future studies of the structural, electronic, and optical properties of 2D hexagonal SnS$_2$ and orthorhombic SnS and may offer important guidance for realizing SnS$_2$- and SnS-based electronic and optoelectronic devices.

4. Experimental Section

Materials Growth: SnO$_2$ and S powders were used as source materials in a conventional single-zone horizontal quartz tube (1 in.) furnace. In a typical experiment, SnO$_2$ (=15 mg) powders in a quartz crucible were placed in the center of the tube furnace. Also, S (=350 mg) powders in a quartz crucible were placed 13 cm upstream from the center of the tube furnace. The degenerately boron-doped (0.001–0.005 13 cm) furnace was kept at 705 (1°C). Also, S powder was measured to be 350 °C for 40 min, respectively. The measured probe size was ≈0.8 Å.

UPS Characterization: UPS characterization was carried out by using a Kratos AXIS ULTRADLD XPS system equipped with a He I of UV source. The aperture for UPS has a diameter of 110 µm. Vacuum pressure was kept below 3 × 10$^{-8}$ torr, and neutralizer was applied during the data acquisition. For UPS spectra comparison, commercial available bulk SnS$_2$ crystals (2Dsemiconductors Inc.) were used.

Additional Characterizations: Microstructural analyses were done by a FEI NNS450 SEM. Optical microscopy analyses were performed with a Nikon Y-Fl optical microscope. Raman spectra were collected using a Horiba system with a 532 nm laser (=2 mW excitation power, 100× objective lens). For Raman spectra comparison purposes, commercial available bulk SnS$_2$ crystals (2Dsemiconductors Inc.) were used. All Raman spectra were calibrated using the 520.5 cm$^{-1}$ line of a Si wafer. Thickness measurements were performed using Veeco Dimension 5000 AFM in tapping mode.

Calculations: The calculations were based on the first-principles DFT and density functional perturbation theory using the projector augment wave method as implemented in the software package VASP[42]. For the electronic structure calculations, a Monkhorst–Pack scheme was adopted to integrate over the Brillouin zone with a k-mesh of 12 × 12 × 8 (8 × 8 × 1) for the bulk (few-layer) structures. A plane-wave basis kinetic energy cutoff of 500 eV was used. vdW interactions in bulk and few-layer SnS$_2$ were accounted for using a semi-empirical correction to the Kohn Sham energies when optimizing each structure.[43] The optimized lattice constants for bulk SnS$_2$ and SnS were $a = 3.70$ Å, $c = 11.85$ Å and $a = 4.35$ Å, $b = 3.99$ Å and $c = 11.21$ Å, respectively. This study used the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional to obtain accurate values for the bandgaps and ionization potentials for each phase.[44] The HSE calculations incorporated 25% short-range Hartree–Fock exchange and the screening parameter was set to 0.2 Å$^{-1}$. Calculations of the vibrational frequencies at Γ point relied on density functional perturbation theory.

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