



Atomic Layer Deposition Mechanisms and Crystal Structures of Tin Sulfide & Other Issues Related to Tin Sulfide Solar Cells

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**Atomic Layer Deposition Mechanisms and Crystal Structures of Tin Sulfide
& Other Issues Related to Tin Sulfide Solar Cells**

A dissertation presented

by

Xizhu Zhao

to

The School of Engineering and Applied Sciences

in partial fulfillment of the requirements

for the degree of

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in the subject of

Applied Physics

Harvard University

Cambridge, Massachusetts

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Atomic Layer Deposition Mechanisms and Crystal Structures of Tin Sulfide & Other Issues Related to Tin Sulfide Solar Cells

Abstract

Tin monosulfide (SnS) has been investigated as a solar cell absorber due to its suitable bandgap and high absorption. The optoelectronic properties of SnS are largely dependent on its microstructure and deposition methods. First, we review the experimental and theoretical studies on SnS since the mid-20th century and evaluate the results with a focus on the deposition methods and microstructures; we also summarize the major challenges facing the SnS solar cells.

To advance our understanding of the material fundamentals, we study the ALD growth behavior and mechanisms of SnS using a new and highly reactive liquid tin (II) precursor. Pure and stoichiometric SnS films can be obtained in the range of 65 – 180 °C. Mechanistic studies suggest higher probability of a double ligand-exchange process (“Sn-bridge” formation) in the Sn-precursor exposure step and dissociative or associative chemisorption of H₂S in the following step. Solar cells fabricated using the SnS film deposited using this new precursor show comparable cell efficiency and improved device yield. We also study the crystallographic phases and orientations of the ALD-SnS thin films, which depend on the deposition temperature, film thickness, and choice of substrate. We confirm the presence of the metastable cubic π -SnS and find that it is more favorable at lower deposition temperatures. Relatively thick films grown on both silicon thermal oxide and NaCl (100) substrates contain mixed π and α phases and are textured, with the latter showing much higher degree of texturing and a different orientation. The π -SnS converts to α -SnS after annealing, consistent with the π phase being metastable. In

addition, we demonstrate a proof-of-concept solar cell device made from the highly oriented SnS grown on NaCl.

Finally, we delineate several additional approaches to understanding and improving the SnS solar cells by addressing different layers of the device, including the back-contact resistance, alternative absorbers, buffer layer doping, and addition of an anti-reflection coating, which has led to an increase the photocurrent and a new record efficiency of 5.2% (uncertified).

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1 Chapter 1 Introduction

Few would doubt that the semiconductor is a major pillar of our modern civilization. Given the ever-increasing demand for computing, storage, and communication, especially with the recent focus on artificial intelligence and crypto currency, the global market for these semiconductor-based electronics keeps growing at a high speed and has exceeded \$400 billion in 2017¹, which equals 0.5% of the global GDP² of that year. Although one often refers to the electronics sector only when talking about the semiconductor industry, energy conversion is the other major application of semiconductors. Photovoltaics (PV) are enabled by the unique properties of the p-n junction, which allows the excess electrons and holes created by photon-excitation to move in different directions and thus can be collected by an external circuit. With the increasing demand for energy and concerns over climate change, renewable energy with low carbon footprint is the only way to go. PV is a major component as well as the fastest growing one among all types of renewable energy³. Although the market value has seen a decrease in recent years due to decreasing price, the installed capacity keeps growing at high speed⁴, which means an ever-increasing demand for PV materials.

A semiconductor has a small to intermediate bandgap and shows a temperature dependence of conductivity generally opposite to that of metal, as opposite to a metal, which has overlapping conduction and valence bands, or an insulator, which has a large bandgap. The

¹ <https://www.statista.com/statistics/266973/global-semiconductor-sales-since-1988/>

² <https://www.statista.com/statistics/268750/global-gross-domestic-product-gdp/>

³ <https://www.iea.org/newsroom/news/2016/july/renewable-energy-continuing-to-increase-market-share.html>

⁴ <http://markets.businessinsider.com/news/stocks/solar-pv-modules-update-2017-global-market-size-competitive-landscape-key-country-analysis-and-forecast-to-2021-1013095481>

conductivity of a semiconductor is caused by excitation of electrons into electron-hole pairs, where the electrons are excited across the bandgap into the conduction band while holes remain in the valence band. There exist two different types of conductivity in a semiconductor, p-type where conductivity is dominated by holes in the valence band and n-type where conductivity is dominated by electrons in the conduction band, caused either by intrinsic defects or by external doping. When the two types of semiconductor are put together, a p-n junction is formed, which is a diode that lays the foundation to electronic and photovoltaic devices.

To meet the increasing demand for electronics and energy, we need to develop semiconductor materials that are low-cost, earth-abundant, and non-toxic. Silicon is the most widely used material for both electronics and photovoltaics, but it has certain drawbacks. Particularly for solar cell absorber, it has a relatively low absorption coefficient due to its indirect bandgap, thus one generally needs more than 200 μm of Si to efficiently absorb the light. This leads to stringent requirements on material quality (high-purity and single-crystalline Si is preferred) to allow a long carrier diffusion length for the carriers to travel through the absorber and be collected. Other materials such as gallium arsenide (GaAs), indium phosphide (InP), cadmium telluride (CdTe), and copper indium gallium selenide (CIGS) are also popular semiconductor materials, each being particularly useful in certain applications. CdTe and CIGS based solar cells have reached more than 20% efficiencies and full commercialization with cost comparable to Si solar cells. However, their future for supplying a major fraction of the world's energy use is limited by the toxic or rare elements in their composition. Considering supply and toxicity issues, tin-monosulfide (SnS) has caught our interest as an alternative semiconductor material particularly promising for solar cell applications due to its suitable bandgap, high absorption, and binary composition of only abundant and non-toxic elements.

In this chapter we review the experimental and theoretical literature on SnS since the mid-20th century and evaluate the factors that affect the microstructures and optoelectronic properties of SnS, such as deposition methods and conditions. We also revisit some earlier discussions of cubic SnS, in light of the recently discovered cubic π phase, to consolidate the inconsistent reports in literature. In the end, we outline the approaches taken in this work to advance the understanding of material fundamentals and improve SnS solar cell device performance.

1.1 Development of and challenges facing SnS

Both elements in SnS are abundant in the Earth's crust and are already integral parts of our modern industrial chain, which renders significant advantage over materials such as the gallium or indium-containing semiconductor materials. The binary nature of SnS also significantly reduces the phase complexity compared to some other common ternary or quaternary materials such as CIGS. Yet, the multi-valence transition metal nature of tin still introduces enough complexity that makes the phase study of SnS less than straightforward. Simply speaking, there exist several binary compounds of tin and sulfur: SnS, Sn₂S₃, Sn₃S₄, and SnS₂, and even when we have an equal amount of Sn and S with pure Sn²⁺, there are still several different phases that can undergo transition with change in temperature and pressure as shown in the temperature – composition (T-x) phase diagram, [1, 2] as well as several metastable phases with relatively similar energy of formation that exist or co-exist under moderate synthetic conditions. [3, 4]

Early studies SnS focused on its bulk thermodynamic and optoelectrical properties as compared to the then more popular isotropic cubic semiconductors such as lead sulfide (PbS) or tin telluride (SnTe) and established the phase diagrams and the crystal structures of the

thermodynamically stable phases of SnS. [1, 5-10] But such results of SnS in the thin film format is less conclusive. The experimental structural and optoelectronic properties of SnS thin films reported in literature vary across a wide range depending on the deposition or characterization methods. In addition, the theoretical studies based on density function theory (DFT) have been especially challenging due to its distorted crystal structure and the existence of the van der Waal bonds caused by the lone pair of electrons on the Sn^{2+} . [11-17]

A major finding recently on SnS is a new crystal structure with a 64-atom cubic unit cell, the presence of which has since been confirmed with experiments and simulations. [4, 16, 18-25] But limited information about the formation conditions or material properties exists for this phase other than some x-ray or electron diffraction studies and absorption studies.

The photovoltaic potential of SnS has been explored since the 1990s and first realized in Noguchi's solar cell device with a measurable 0.29% efficiency in 1994. [26] There are only a handful of academic research groups that have experimented with developing SnS solar cells. The efficiency reached 1.3% in Reddy's device in 2006 [27] and over 5% in the past few years with the continuous efforts by the Gordon Group at Harvard University and the Buonasissi Group at MIT in the past few years. [28-30]

Literature reviews on SnS are rare [31, 32] and especially lacking is one that synthesizes the recent development with previous findings regarding the crystal phase and deposition conditions. Thus, this chapter aims to provide a comprehensive overview of the literature with focuses on the phases and microstructures of SnS and the various synthetic methods. The electrical and optical properties, film morphology, and device performance will be addressed briefly as appropriate.

1.2 Synthetic methods

There are many ways of making SnS thin films. The Bridgeman-Strockbarger or similar high temperature processing methods were used for bulk single crystal growth, which has been well reviewed by Banai et al. [31] and will not be further address here. For thin film deposition, most researchers used either vacuum deposition methods, which include thermal evaporation (TE), [24, 26, 30, 33-50] atomic layer deposition (ALD), [23, 28, 29, 51-56] pulsed laser deposition (PLD), [13, 57, 58] sputtering, [59] e-beam evaporation (EE), [60] molecular beam epitaxy (MBE), [61] and tin sulfurization; [62, 63] or solution processing methods, which include chemical bath deposition (CBD), [20, 22, 64-69] spray pyrolysis, [27, 70] and successive ion layer adsorption and reaction (SILAR). [71, 72] Nano-particles of SnS have also been synthesized by CBD, [16, 19, 73-76] thermal-decomposition, [77] electro-deposition, [78] and chemical vapor deposition (CVD). [79] We can see that the most common method for making the SnS thin films is TE from a SnS target, whereas CBD from Sn and S containing precursors is the most common method for making SnS nanoparticles.

The experimental conditions and main results in literature are summarized in Appendix A. Table A.1 lists the major SnS literature using vacuum deposition except ALD, which is separately listed in Table A.2 since it is the method to make a record SnS solar cells and the method studied in this thesis. Table A.3 lists the major literature on SnS deposited using solution processing methods.

1.2.1 Vacuum deposition methods

Due to the high deposition temperatures and different volatilities of Sn and S, stoichiometry control is a common problem. Especially where elemental Sn and S is used as the starting source, redox reaction happens during the deposition and the films become particularly

susceptible to formation of secondary phases such as Sn_2S_3 , SnS_2 , and Sn_3S_4 . Researchers have put a considerable effort in searching the parameters space to obtain pure SnS, such as the Sn to S ratio in the starting material or the deposition conditions such as temperature. [36, 37, 46, 62, 63] Thermal evaporation (EE) has been the most commonly used method for making SnS thin films, which deposits SnS from either reaction of elemental Sn and S vapors or from SnS vapor generated by heating the source/target; thus, it is sometimes also called vapor transport deposition (VTD). A few groups have used PLD and MBE for finer control of film growth, but those methods are much slower and only very limited discussion on the impact deposition parameters on film properties can be found. [13, 57, 61]

Reasonably stoichiometric SnS films made using vacuum deposition are usually of the order of 100 nm – 1 μm in thickness and deposited at temperatures mostly between 150 °C to 450 °C. Film properties, such as crystal structure, morphology, bandgap, and conductivity, often exhibit certain changes with the deposition parameters, especially temperature, although the actual values vary considerably from study to study as can be seen in Table A.1. Most studies show that the Sn/S ratio tends to increase slightly as temperature increases, and the trends in the microstructure and other properties will be discussed in the respective sections below.

1.2.2 Atomic layer deposition

The record SnS solar cells to date are deposited using ALD, which has an efficiency of 4.4% [29] due to its ability to make pure stoichiometric and conformal films. High quality SnS can be obtained by selecting the appropriate precursors with only Sn^{2+} and S^{2-} , and in an oxygen free environment at relatively low temperatures, which gives excellent elemental purity and is less susceptible to formation of the Sn_2S_3 , SnS_2 , and Sn_3S_4 phases. And the layer-by-layer process of ALD allows each layer/atom to find its equilibrium position and thus likely results in

less defect formation. More details of the ALD process can be found in Chapter 2. In addition to high quality films, ALD also allows precise film thickness control, conformal coating of high-aspect ratio features, and can be potentially adapted for CVD for industrial level fabrication.

Several metal-organic Sn(II) compounds has been used as precursors for SnS ALD, including tin(II) acetylacetonate, $(\text{Sn}(\text{acac})_2)$ [23, 51, 54], bis(1-dimethylamino-2-methyl-2-propoxy)tin(II), $(\text{Sn}(\text{dmamp})_2)$ [55], bis(N,N'-diisopropylacetamidinato)tin(II), $(\text{Sn}(\text{A-amd})_2)$ [28, 29, 52], and tetrakis(dimethylamino)tin(IV), (TDMASn). [53] The deposition temperature is less than 300 °C and the thickness studied is less than 50 nm, except for studied by Sinsermsuksakul et al. [28, 29, 52] Again, changes of structural and optoelectronic properties with deposition parameters will be discussed in the later sections.

1.2.3 Solution processing methods

Both SnS thin films [20, 22, 27, 64-72] and nanoparticles [16, 19, 73-79] have been successfully synthesized using solution-processing methods. Stoichiometry is again a major problem for the solution-processed SnS thin films, as well as oxygen incorporation from the non-oxygen-free deposition environment. There are many different Sn and S precursors, organic or inorganic, as well as different chelating agents or surfactant/capping agents, all of which affect the crystal structure, morphology, and properties of SnS films or nanoparticles (see Table A3 in Appendix A for a quick summary). Yet there is no conclusive view on the effect of chemicals and this topic will not be discussed in the scope of this chapter.

The deposition temperature is generally lower than in that in the vacuum deposition case, and a considerable fraction of the SnS were deposited below 100 °C, but an annealing step up to 400 °C was more often adopted for recrystallization or grain growth. And the nanoparticle sizes or film thicknesses are often on the order of 10 nm to 100 nm, and more structural characteristics

such as TEM are available for the nanoparticles possible due simpler sample preparation. Again, details of the structural and optoelectronic properties and their dependence on temperature will be discussed in the later sections of this chapter.

1.3 SnS microstructures

The tin-sulfur system has several compositions (SnS , Sn_2S_3 , SnS_2 , Sn_3S_4) and many different crystal structures/phases. The T-x phase diagram has been established by earlier experimental studies from 1909 to 1986 using bulk SnS and by simulations, which is well summarized by Banai et al. [31]. The effect of sulfur pressure (P_{S_2}) was also studied by Albers et al. [1] and the P_{S_2} -T and P_{S_2} -x relations were obtained over various solid-liquid-vapor three phase equilibria of the Sn-S system, but note that there were also seemingly contradictory results reported from that time [8]. In scope of this thesis, we will focus only on SnS.

1.3.1 Stable crystal structures of SnS

It has been well-established that the orthorhombic SnS (α -SnS) is the thermodynamically stable phase up to 600°C.[1, 31] A solid phase transformation from the orthorhombic α -SnS to a pseudo-tetragonal one (β -SnS)⁵ occurs at about 600°C, which is well described by Wiedemeier et al., [9]. The lattice constants of the α -SnS are most commonly reported as $a = 4.33 \text{ \AA}$, $b = 11.19 \text{ \AA}$ and $c = 3.98 \text{ \AA}$ at room temperature, as listed in the powder diffraction file of SnS from the crystallography database (PDF 00-039-0354). As temperature increases, the lattice constants b and c expand while a contracts until a and c become equal at 4.16 $\text{\AA}$, and above 600 °C, a , b , and c increases together with temperature. Since the SnS thin film deposition or processing

⁵ It worth noting that this β -SnS is still a double layer formation with a distorted rock-salt structure and should not be confused with later discussions of “rock-salt” structure at low temperatures.

temperature seldom exceeds 500°C, above which sublimation will become a major concern, [10, 80] we will not further discuss the β -SnS or other high-temperature polymorphs in this chapter.

Thin films deposited on substrates often demonstrate a high degree of preferred orientation that is dependent on a range of parameters such as substrate, temperature, and thickness. Most groups have reported either (111) or (040) as the dominating orientation as shown by XRD, which means that the thin films have crystallites lying with the {111} or {010} planes parallel to the substrate. Often, the (111) peak is seen to dominate films deposited at lower temperatures while the (040) peak dominates films deposited at higher temperatures or after annealing; the exact transition temperature varies depending on deposition methods and other parameters, but generally a clear transition can be seen from between 100 °C and 300 °C. [24, 26, 36, 39, 43-45, 48, 55, 58, 61] Hartman et al. [59] shows that the preferred orientation of sputtered α -SnS is (111) when using higher Ar pressures but (002) using lower pressures. The orientation is also shown to be dependent on and substrates, where the Au [56] or Si [38] substrates induce more of the (040) peak growth; and epitaxy growth in the (040) direction has been reported on single-crystal NaCl and MgO substrates as well as on graphene-mediated substrates. [34, 35, 48, 57, 61]

Grain size has been another point of interest in SnS film studies. There are two ways of describing the grain size, one is by looking at the morphological grain by SEM or AFM, and the other by estimating from the FWHM of the XRD peaks using the Scherrer equation. Note that these two methods are not equivalent: SEM or AFM reveals the macroscopic grain shape and size; while the Scherrer equation is sensitive to the crystallographic domains and the linear and planar defects. Therefore, the size obtained from the Scherrer equation is generally much smaller

than that from SEM or AFM. To avoid confusion, in this work the size estimated from SEM will be referred to as “grain size” and that from the Scherrer equation as “crystallite size”.

1.3.2 Metastable phases of SnS

Besides the α -SnS and β -SnS that have been established as the thermodynamically stable phases at low and high temperatures, there are a few other cubic crystal structures that have been reported since the 1960s for SnS in the thin film or nanoparticle format, which could be results of film formation under non-equilibrium conditions such as external stress or in-situ kinetic barrier. Badachhape et al. [33] seems to be the first to report a cubic phase of SnS in 1962, where the film was epitaxially grown on NaCl (100) using the vapor deposition method; they carried out an electron diffraction study and assigned a structure observed approximately 400 °C to zinc-blende, and the lower temperature to orthorhombic. Bilenkii et al. [35] reported in 1968 a similar orthorhombic to cubic transformation happening above 500 °C, but they assigned the cubic phase to rock-salt with $a = 5.80 \pm 0.02$ Å. Wiedemeier [9] rationalized the transition from orthorhombic to cubic at high temperatures using the theory of decreasing orbital hybridization at higher temperatures, and estimated the cubic lattice parameter to be 5.84 Å from the known cubic structures of GeSe, GeTe, SnSe, and SnTe.

However, in later literature, the cubic phase SnS is only reported to form at relatively lower deposition temperatures and transform to orthorhombic as temperature increases. [16, 18-20, 22-24, 55, 65, 66, 68, 75, 79] Few cases of cubic SnS have been seen in vacuum deposited SnS due to the often high deposition temperature used, except for a recent study by Hara et al.. [24] Most cubic SnS films or nanoparticles are deposited using CBD at temperatures often less than 100 °C. Most reports assign these low-temperature cubic films or nanoparticles to the zinc-blende crystal structure with a lattice constant $a = 5.845$ Å [75] or 5.783 Å [65].

It would be reasonable to suggest that the low temperature cubic-SnS is fundamentally not the same as the high temperature cubic-SnS as discussed in the previous two paragraphs and should not be confused. Yet, note that an outlier exists in [34], which reports a rock-salt SnS film evaporated at a relatively low temperature of 150 °C on NaCl, and a transformation from a mixture of orthorhombic to pure rock-salt as temperature increases, which has a lattice parameter of $a = 6.00 \text{ \AA}$ that is much larger than other reports.⁶

1.3.3 A new cubic phase π -SnS

Until recently, the confusion over the low temperature cubic-SnS lies in the assignment of whether it is rock-salt or zinc-blende. Given the same lattice constant, the only difference between the zinc-blende and rock-salt SnS that can show up in their XRD patterns is their relative peak intensity of samples with random orientation, while the peak positions are the same. [3] However, in experimental works the random orientation condition is not always practical, and the relative intensities are seldom discussed. In addition, peaks that do not correspond to any of the rock-salt or zinc-blende phases were sometimes also observed and were often assigned to a Sn_xS_y or Sn_xO_y phase without much deliberation. Therefore, it would not be unreasonable to remain critical about those assignments and keep searching for a better solution.

In 2015, Rabkin et al. [19] reported a new 64-atom unit cell cubic phase, which could be the solution to the long time confusion of the cubic structure observed in earlier literature. In their solution synthesized SnS nanoparticles, Rabkin found that a small fraction had a tetrahedron shape that was clearly different from the usual platelet shape of the α -SnS. Both the

⁶ Mariano et al., studied both SnSe and SnS. SnS film of 100 nm was evaporated onto NaCl substrate and reported to be epitaxial and have a rock-salt structure. The electron diffraction patterns that would support their claim were only presented for SnSe in the paper.

morphology and the XRD spectrum were similar to those reported by Greyson, but they were not satisfied with assigning it to the zinc-blende phase as many previous authors. They confirmed the 1:1 stoichiometry with TEM-EDS and took a series of off-axis process electron diffraction (PED) patterns from a single nanoparticle with small angular steps, reconstructed the reciprocal space, and obtained a structural solution with a lattice parameter of $a = 11.658 - 11.801 \text{ \AA}$ and 64 atoms in a unit cell. They inferred that this phase is of cubic structure with $a \sim 11.7 \text{ \AA}$. And from analysis of apparent and missing symmetry in their PED patterns, they concluded that the $P2_13$ space group is the only reasonable one to assign their SnS to, which they called π -SnS.

Abutbul et al. [20] and Skelton et al.[4] later provided complementary XRD characterizations and DFT simulations of formation energy and band structure. The different unit cells of SnS as well as the ground state structures of Sn_2S_3 and SnS_2 are well summarized in [4] and illustrated in figure 1.1. The XRD spectrum shows that π -SnS has peaks close to all peaks of the rock-salt or zinc-blende SnS, plus several additional peaks. In light of this, the assignment of either rs- or zb-SnS in earlier experimental works should likely be reassigned to.

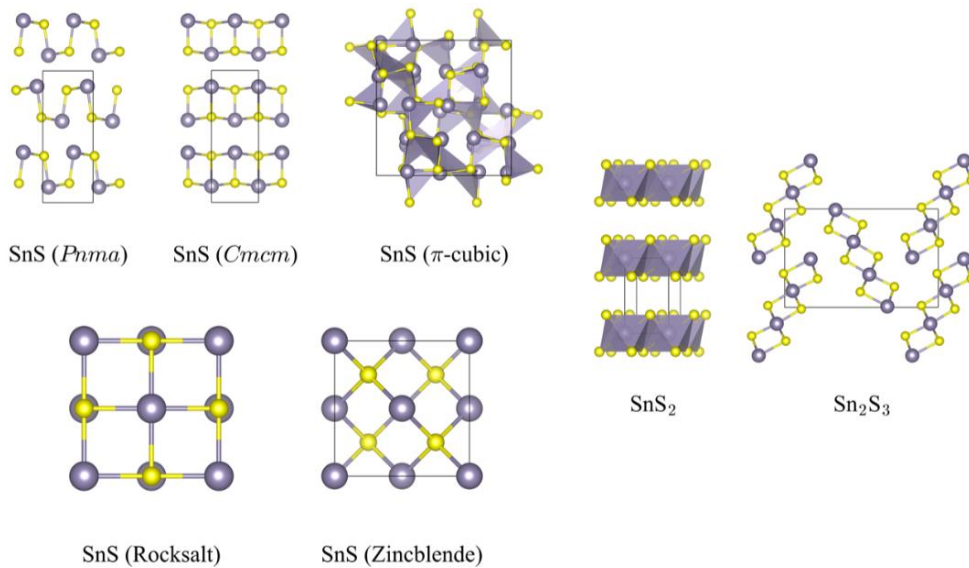


Figure 1.1 Illustrations of the SnS crystal structures most cited and the ground states crystal structure of Sn_2S_3 and SnS_2 . Reproduced from [4].

1.3.4 Addition considerations in XRD studies of SnS crystal structure

Although one would think the difference between orthorhombic and cubic should be clear, as well as the preferred orientation, the assignment of XRD peaks could be quite complicated due to several reasons. First, many characterizations were done on sample prepared under non-stoichiometric conditions or with significant chance of incorporating oxygen, which could lead to mixed phases of SnS and Sn₂S₃, SnS₂, or SnO₂, which in turn results in XRD peaks that could confuse the assignment.⁷

Second, the reported cubic structures are mostly for thin films, which often grow at certain preferred orientation/texturing on substrates and are characterized with XRD. But the most commonly used XRD θ – 2θ scan is in the powder mode (0D or 1D) and only able to detect crystal planes parallel to the substrate. Advanced XRD techniques such as GIXRD or 2DXRD can characterize all orientation/texturing of the thin film, but the set-up is not always available. From close examination of the literature, we believe the XRD were conducted in powder mode unless otherwise specified. The film texturing would cause the number of observed XRD peaks to be significantly less than the number of peaks in the reference PDF cards, which give us much less confidence in phase identification. Therefore, unless the sample is itself a powder sample guaranteeing random orientation, or examined using GIXRD or 2DXRD, one cannot rule out certain phases just because it does not show up in the XRD scans.

To make it worse, the cubic peaks lie close to the orthorhombic ones, especially for the strong intensity peaks that are crowded in the region of $30.4^\circ - 32.7^\circ$, with some as small as only 0.1° apart, testing both the resolution limitation and the calibration/alignment of some XRD

⁷ For example, the earlier report of the zinc-blende SnS nanocrystals by Greyson et al. left a few prominent XRD peaks unexplained.

instruments (i.e. $31.5^\circ/31.9^\circ$ ⁸ for α -SnS and 31.8° for cubic-SnS). Therefore, without multiple peaks confirming certain phases, or additional characterization methods, it is not unexpected that mis-assignment of phases or orientations could occur.

1.4 Thermodynamic properties

1.4.1 General properties

Thermodynamic properties have been well established for bulk SnS from earlier studies. The SnS crystals were mostly grown using high temperature annealing of elemental Sn and S, and the thermodynamic measurement was taken by measuring the temperature dependent mass change and analysis of the gaseous species using mass spectrometry.[6, 8, 10] For those reasons, the accessible phases of SnS are the thermodynamically stable ones (α -SnS at low temperature and β -SnS at high temperature). Experimental measurement of those properties such as the enthalpy of formation from other less stable phases or thin films is difficult, and we have yet to see any such report. Despite possible differences can be caused by the reduced dimension, the thermodynamic properties should not differ much, and the normal thickness used for the SnS solar cell, which is at least a few hundred nanometers, can be reasonably approximated with the bulk properties of the same phase.

The melting temperature of SnS was found to be 881.5°C . [1] The enthalpy of formation, $\Delta H_{298}^\circ(\text{f})$, was reported by Wiedemeier et al. [10] to be $-102.9 \pm 4.0 \text{ kJ/mol}$, and others also reported enthalpy of formation between -100 and -108 kJ/mol . [31] The dissociation energy (D_0°) of SnS (g) was reported by Colin et al. [8] to be $460.7 \pm 12.6 \text{ kJ/mol}$. The enthalpy of

⁸ Note that the α -SnS (040) and (031) peaks almost overlap, but the (031) is often not addressed and not shown in the most-cited reference PDF 00-039-3954.

sublimation (ΔH_{298}°) of $\text{SnS}_{(s)} \rightarrow \text{SnS}_{(g)}$ was calculated by two independent groups [8, 10] to be 220 kJ/mol using mass spectrometer and Knudsen effusion cell.⁹ From the mass spectrometry of the sublimed vapor, Colin et al. [8] found that the solid SnS sublime as both SnS and Sn_2S_2 in the temperature range of 542 °C – 732 °C, and Wiedemeier et al. [10] observed considerable mass loss starting from 460 °C. Since sublimation of the material is undesirable in device fabrication, this put an upper limit on the processing temperature for SnS solar cell. Note that if we can maintain a high vapor pressure of SnS, we should be able obtain desirable recrystallization and grain growth at high temperatures. Yet, experimental annealing studies has shown deteriorated morphology upon annealing temperatures above 500 °C despite efforts in maintaining vapor pressure.[80]

1.4.2 Phase stability

With recent advances in computing power and renewed interest in SnS a PV material, several theoretical works have been done to evaluate the phase stability.[2-4, 11-17, 25, 81-85] Theorists generally agree that α -SnS is the most stable phase at temperatures < 600°C, which has an orthorhombic unit cell with double-layers connected by van der Waals forces. Burton et al. [3] performed total energy calculation using DFT-PBESol and GGA with geometry relaxation for the α , β , zinc-blende, and rock salt phases of SnS, as well as the ground state structures for Sn_2S_3 and SnS_2 . The dynamic phase stability was also assessed in the temperature range of 300 – 1000K. They found that the zinc-blende SnS has an enthalpy of formation roughly 71.5 kJ/mol higher than the α -SnS phase, which indicates that the zinc-blende SnS is practically inaccessible. The calculated equilibrium lattice constants of zinc-blende SnS also does not agree with the

⁹ $\Delta H_{298}^\circ = 220.1 \pm 6.7$ kJ/mol from Colin and 220.4 ± 3.0 from Wiedemeier.

experimental value, although the same model results in reasonable agreement with experiments for all other phases. The enthalpy of formation for rock-salt SnS was calculated to be 7.7 kJ/mol higher than α -SnS, showing that the previously assigned zinc-blende phase should be in fact rock-salt.¹⁰

However, this argument would undergo modification considering the recently resolved π -SnS phase, which has been assigned to the cubic space group $P2_13$ and can be seen as a distorted large rock-salt structure with 64 atoms in its unit cell. Abutbul et al.[20] and Skelton et al. [4] are the only authors to date that reported thermodynamic calculations of π -SnS. DFT total energy calculation from [20] shows that the total energy is -27.497 Ry¹¹ per atom pair for π -SnS, which is meaningfully lower than the -27.493 Ry calculated for the ideal rock salt structure. The total energy calculated for α -SnS is -27.498 Ry, which is only slightly more stable than the π phase. DFT calculation from [4] reported the π -SnS sits at 2.19 kJ/mol above the α -SnS, which is comparable to the 0.004 Ry (1.35 kJ/mol) calculated in [20]. They also predicted the rock-salt phase to sit 6.6 kJ/mol and 8.5 kJ/mol above the α phase respectively, consistent with Burton's earlier result [3]. The lower energy of π -SnS compared to rs-SnS were ascribed to the hybridization of the Sn 5s² and 5p⁰ [4] which lowers the energy of the system but is forbidden in the rock-salt symmetry. This small difference between the α -SnS and π -SnS indicates high likelihood of the π

¹⁰ No experimental enthalpy of formation is available for the cubic phases of SnS.

¹¹ Conversion: 1 Ry = 13.6057 eV and 1 eV = 96.485 kJ/mol. Thus π = -374.116 eV = -36096.697 kJ/mol, rs = -374.061 eV = -36091.391 kJ/mol, and α = -374.130 eV = -36098.048 kJ/mol.

phase formation.¹² In light of this, it is possible that the assignment of either the rock-salt or the zinc-blende SnS in earlier experimental works should instead be viewed as π -SnS.¹³

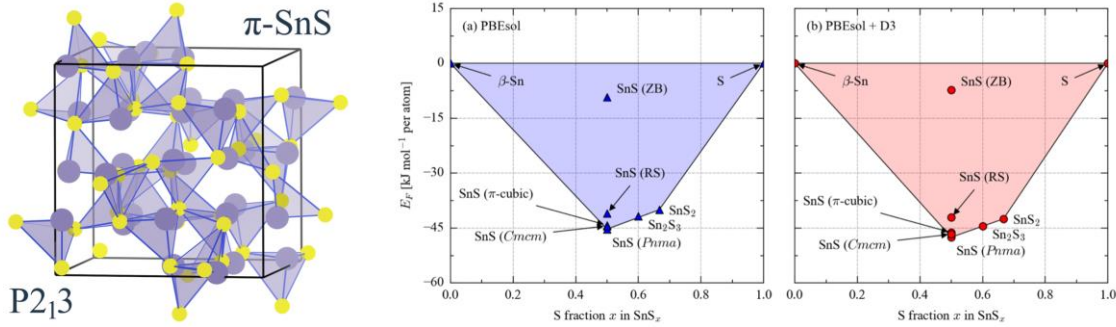


Figure 1.2 Illustration of the crystallographic unit cell of the π -SnS (a) and calculated formation energy for different phases of the Sn_xS_y system (b). Reproduced from [4].

1.4.3 Orientation and surface energy

Another factor in crystal structures worth addressing is the anisotropy in the α -SnS, which could result in different band position and surface energy that can impact film growth and subsequently device performance. Although it is well-known that surface energy differs for different facets of a crystal, little work has been done on SnS. It is well known that the surface free energy ranking for a cubic structure follows $(110) > (100) > (111)$ in a FCC crystal and $(111) > (100) > (110)$ in a BCC crystal, and the α -SnS is qualitatively more similar to a FCC crystal. There is only work found that studies the surface energies and the positions of the

¹² One way to think about energy sizes is using the Boltzmann distribution. If each pair of phases was treated as energy levels, Boltzmann would predict ca. 13 % rs-SnS at 298 K vs. π -SnS, and ca. $4\text{e-}10$ % zb-SnS at 298 K vs. rs-SnS.

¹³ Note this reinterpretation of the rock-salt SnS to π -SnS is much less certain than the reinterpretation of all the zinc-blende SnS reports as either rock-salt or π -SnS, owing to the much smaller energy difference between rock-salt SnS and π -SnS (ca. 5 kJ/mol) than between rs-SnS and zb-SnS (ca. 65 kJ/mol).

conduction band minimum (CBM) and valence band maximum (VBM) of the different facets of α -SnS [85], and there is no such work found on cubic-SnS.

Their calculation shows that (100)¹⁴ has the lowest surface energy, which is not surprising giving that the double layers are only weakly bonded by van der Waal forces and no dangling bonds results from exposing the surface. It also has a conduction band position of 3.8 eV, which is the value cited in Niall's modeling work on SnS solar cells [86]. However, most other major facets have CBM lying between -4.0 eV and -4.2 eV with a couple of exceptions lying even lower at -4.4eV to -4.6eV (120, 110, 021). Based on this calculation, we list the planes that are often mentioned in XRD studies in the order of increasing surface free energy, using the labeling convention of α -SnS XRD peaks in this work: (040) (120) (111) (200) (110) (131) (110) (112) (211) (210) (021) (002).¹⁵ This surface free energy rank agrees with the observation that almost all nano particles of α -SnS have {040} as the largest exposed surface [76, 78] and might also be useful in explaining the texturing and orientation change in the SnS thin films, where a the (111) and (040) peaks are most often reported as the preferred orientation, although as for which one is closely dependent on the deposition method, temperature, and film thickness etc.

¹⁴ This would be the (040) plane in the naming convention of XRD peaks adopted in this thesis (In Stevanovic et al.: a>c>b; this thesis: b>a>c)

¹⁵ Corresponds to (100) (201) (111) (002) (011) (311) (101) (121) (112) (102) (210) (020) in [85].

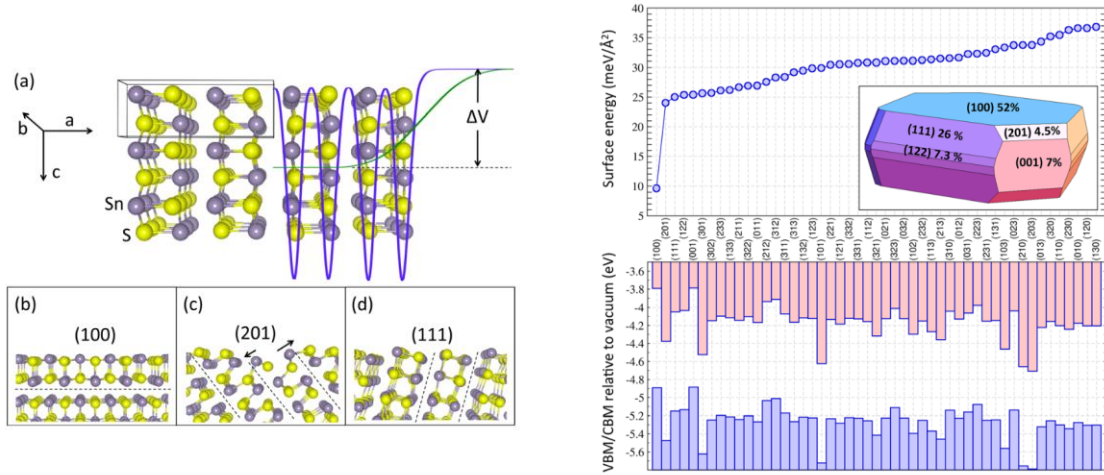
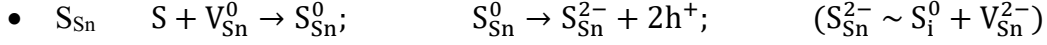


Figure 1.3 Ground state orthorhombic structure of SnS (a) and its calculated surface energies and band positions (b). Reproduced from [85].

1.4.4 Defects

Defect formation in SnS is another subject studied by theorists. Defects are important in determining the electrical properties such as the carrier concentration and carrier lifetime, which are especially critical for PV or other semiconductor applications. Few groups have performed calculations on the defect energy of SnS and most of the works available are on the native defects of α -SnS. There are 6 basic intrinsic defects in α -SnS: Sn vacancy (V_{Sn}), S vacancy (V_S), Sn interstitial (Sn_i), S interstitial (S_i), Sn-on-S antisite (Sn_S) and S-on-Sn antisite (S_{Sn}), and their formation equations are shown below:

- V_{Sn} $Sn_{Sn} \rightarrow V_{Sn}^0 + Sn;$ $V_{Sn}^0 \rightarrow V_{Sn}^{2-} + 2h^+$
- V_S $S_S \rightarrow V_S^0 + S;$ $V_S^0 \rightarrow V_S^{2+} + 2e^-$
- Sn_i $Sn \rightarrow Sn_i^{2+} + 2e^-;$ $Sn_i^{2+} \rightarrow Sn_i^{4+} + 4e^-$
- S_i $S \rightarrow S_i^0 \rightarrow S_i^{2-} + 2h^+$
- Sn_S $Sn + V_S^0 \rightarrow Sn_S^0;$ $Sn_S^0 \rightarrow Sn_S^{4+} + 4e^-;$ $(Sn_S^{4+} \sim Sn_i^{2+} + V_S^{2+})$



Banai et al. [31] reviewed the related works up to 2013. According to those calculations, V_{Sn} transition level lies close to VBM; thus, V_{Sn} acts as a shallow acceptor but V_S is a deep donor and SnS exhibits a p-type conductivity. This is consistent with the experimental result that SnS is a native p-type semiconductor, and consistent with the small activation energy measured in [37, 62].¹⁶ Another main result is that V_S and Sn_S are detrimental mid-gap states that have lower formation enthalpies than V_{Sn} under Sn-rich conditions but have much higher formation enthalpies in S-rich conditions; thus, they can be avoided by having a S-rich environment.

Kumagai et al. [17] published another work on defect formation energy using a modified model with extended Freysoldt-Neugebauer-Van (FNV) correction scheme to account for the anisotropy and the PBE-D3 was used for the exchange-correlation functional because it best reproduced the lattice constant, which the defect formation energy calculation is very sensitive to. They report their result as more similar to that in Malone et al. [84] than in Vidal et al. [13]. The results from both Kumagai et al. [17] and Vidal et al. [13] are shown in Figure 1.4 for illustration.¹⁷ According to the diagrams in Kumagai et al. [17], V_S is hard to eliminate even in S-rich conditions as long as a reasonable p-type conductivity is desired, but the n-type conversion would be more attainable because Sn_i is a shallow donor. They also brought up that Sn_S^{4+} should be treated as a pair of V_S and Sn_i since this splitting lowers the overall energy, and

¹⁶ Yet, there exist some much larger activation energy measurements of 0.15 – 0.45 eV as in Noguchi et al. [27] and Ran et al. [57], which indicates deeper acceptor.

¹⁷ It seems common practice to plot formation energy against Fermi level, which is in turn determined by the type and states of the defects, so the calculation is an iterative process. The charge state of the defect corresponds to the gradient.

Sn_i is likely to locate near V_S . Note that Malone et al. [84] also calculated extrinsic defects of SnS , which will not address in the scope of this chapter.

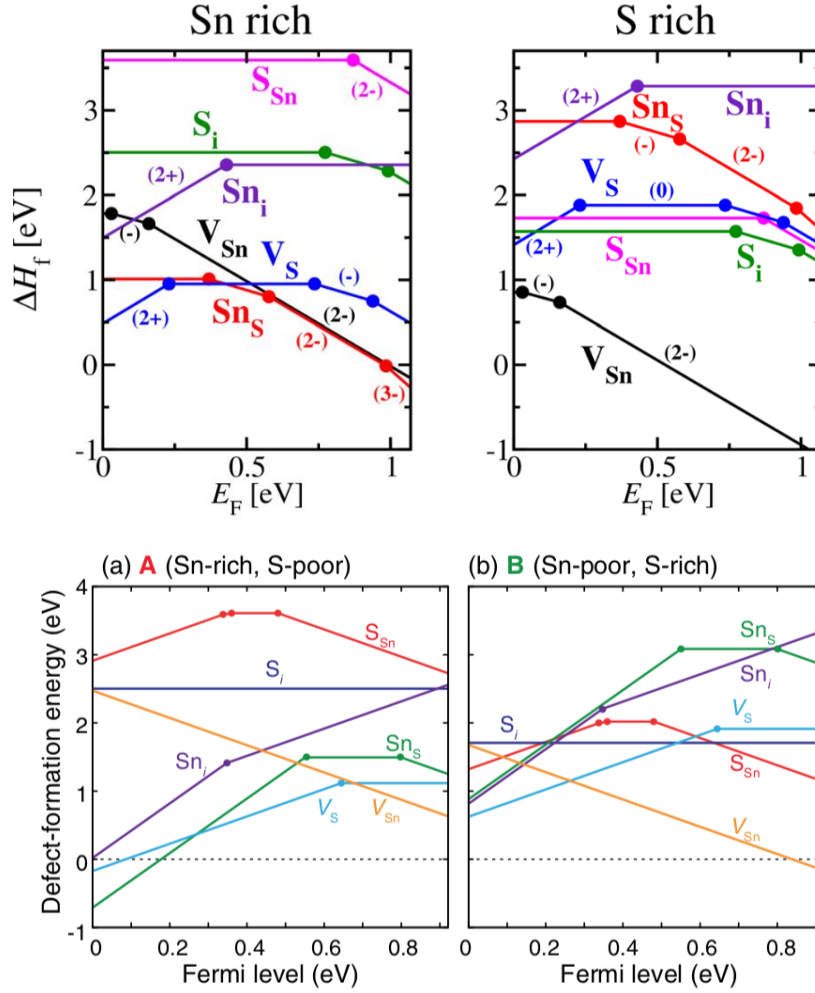


Figure 1.4 Calculated formation energy of different types of intrinsic defects in SnS from two different sources. Upper two diagrams: reproduced from Vidal et al. [13]. Bottom two diagrams: reproduced from Kumagai et al. [17].

1.5 Optoelectronic properties

1.5.1 Band structure

The α - SnS has a complicated electronic band structure due to its low symmetry, double layers connected by van der Waals forces, and large unit cell. Several groups have conducted

band structure calculations on the thermodynamically stable α - and β -SnS using modeling techniques including the ab-initio calculations and the density function theory (DFT). The review by Banai et al. [31] provides a detailed summary of the methods and results from two noticeable works from by Ettema et al. [11] and Lefebvre et al. [12] in the 1990s.¹⁸ Here, I summarize two recent works that have results in reasonable agreement with experimental values.

Vidal et al. [13] performed calculated the band structure, effective masses, and optical spectrum using the VASP code, local density approximation (LDA), and a special GW¹⁹ scheme for accurate bandgap prediction. It reports an indirect bandgap of 1.07 eV, an effective absorption threshold (direct allowed optical transition)²⁰ of 1.5 eV, a dielectric constant of $\epsilon_{\text{inf}} = 13$, and effective masses for electrons and holes along different axis to be $m_{a,h} = 0.33 m_0$, $m_{b,h} = 1.5 m_0$, $m_{c,h} = 0.21 m_0$, $m_{a,e} = 0.2 m_0$, $m_{b,e} = 0.5 m_0$, $m_{c,e} = 0.13 m_0$. Tritsarlis et al. [14] calculated the band structures for single-layer, double-layer, and bulk α -SnS using similar LDA and GW approximations, with a different code (GPAW) for implementing the projected augmented-wave method.²¹ They also used a functional based on PBEsol to correct for the typical bandgap underestimation of the LDA method. The band structure calculated for bulk SnS agrees

¹⁸ In Ettema's calculations for α -SnS, the S $3p_x$ states are covalently bonded to Sn $5p$ states and the $5s^2$ electrons on the Sn atom act as a lone pair pointing towards the interlayer spacing of α -SnS. Ettema predicted the conduction band maximum is at the Γ point while the valence band maximum is not, and SnS has an indirect bandgap smaller than its direct bandgap ($E_{g,\text{ind}} = 1.6\text{eV}$ and $E_{g,d} = 1.8\text{eV}$). Lefebvre confirmed earlier claims that each Sn is covalently bonded to three S atoms and each S atom to two Sn atoms in α -SnS, and the $5s^2$ lone pair cause a small dipole moment between the layers due to the small layer spacing compared to the truly layered material SnO, causing the inter-layer bonding nature to be more than pure van der Waals.

¹⁹ The GW approximation is an approximation made to calculate the self-energy of a many-body system of electrons

²⁰ Note that this is not the same as the electronic direct bandgap. In GaAs, the effective transition threshold is ~ 0.1 eV larger than its direct bandgap.

²¹ Both VASP and GPAW are codes for implementing the projected augmented-wave method, an all-electron method using the frozen core approximation. LDA is used in the exchange-correlation function of the DFT. Another approach is the generalized gradient approximation (GGA). LDA is said to be a better approach for the van der Waals bonded layered crystal structure.

reasonably well with results from Vidal in terms of CBM and VBM positions, the indirect bandgap value, and the effective masses. The dielectric constant for bulk SnS was calculated to be 11.7 – 14.5 for the different axis and methods of approximation, agreeing with another calculation of 11.9 – 12.7 from Banai et al. [15]. It is also shown that the single-layer and double-layer SnS are indirect bandgap materials with bandgap 1.5 eV and 0.5 eV larger than the bulk SnS.

It is generally agreed that the α -SnS CBM lies along the Γ -Y direction with a competing one at the Γ point with a few 10 meV energy difference, while α -SnS VBM lies along the Γ -Z direction, resulting in an indirect bandgap material. We can also see from the band diagram that a local VBM exists along the Γ -Y direction located very close to the global CBM, and a local CBM exists along the Γ -Z direction located close to the global VBM. Thus, α -SnS has direct bandgaps of approximately 1.3 eV and 1.6 eV. The band structure diagram from Vidal et al. [13] is presented below as an illustration. Note although some calculations are in excellent agreement with the experimental optical measurements, the result could be only fortuitous due to the numerous assumptions and approximations in the DFT calculations.

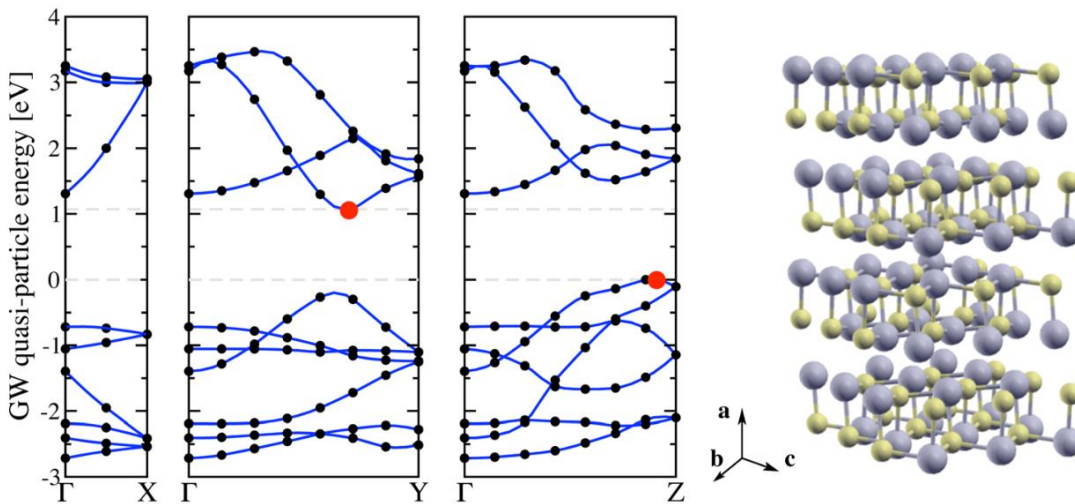


Figure 1.5 Calculated band structure of α -SnS along Γ -X (along **a**-axis), Γ -Y (along **b**-axis), and Γ -Z (along **c**-axis). Large red dots represent valance band maximum and conduction band minimum. Crystal structure of SnS: small yellow spheres represents S atoms, while large grey spheres represent Sn atoms. Reproduced from [13].

Again, little theoretical work can be found about the electronic structure of the π -SnS due to its recent discovery. Abutbul et al.[16] and Skelton et al.[25] are the only ones so far that calculated the electronic structures of π -SnS and other cubic SnS phases.²² Abutbul et al. performed DFT-PBE calculation for the α , π , and rock-salt SnS. The structural relaxation allowed for the π -SnS calculation results in a lattice parameter of 11.885 Å, which is only slightly larger than the experimental value of 11.595 – 11.603 Å obtained by the same research group [19]. Skelton et al.[25] calculated the band structure of π -SnS,²³ and the equilibrium lattice constant was found to be 11.506 Å, slightly smaller than the experimental value. The effective mass was evaluated to be $m_h = 1.22 m_0$ and $m_e = 0.76 m_0$, indicating lower carrier mobility compared to α -SnS [16], and the dielectric constant ϵ_{inf} was found to be 11.5, which is similar to that for the α -SnS [16]. and expected the p-type semiconducting behavior to be unchanged in π -SnS [25]. The energy gap was calculated to be 1.27 eV in [16]²⁴ or 1.72 eV in [25], and the difference between the indirect and direct bandgaps is very small. UV-vis measurement by Abutbul et al.[16] shows indirect bandgap of 1.53 eV for π -SnS, but it is worth noting that those measurements were taken on nanocrystals, which could be different from the thin film or bulk value.

²² Skelton also reported calculated phonon-dispersion modes, which will not be addressed in this review.

²³ using the DFT-PBE methods with the hybrid HSE06 functional to model the electron exchange-correlation.

²⁴ The author commented that underestimation of bandgap is common when using the DFT-PBE methods.

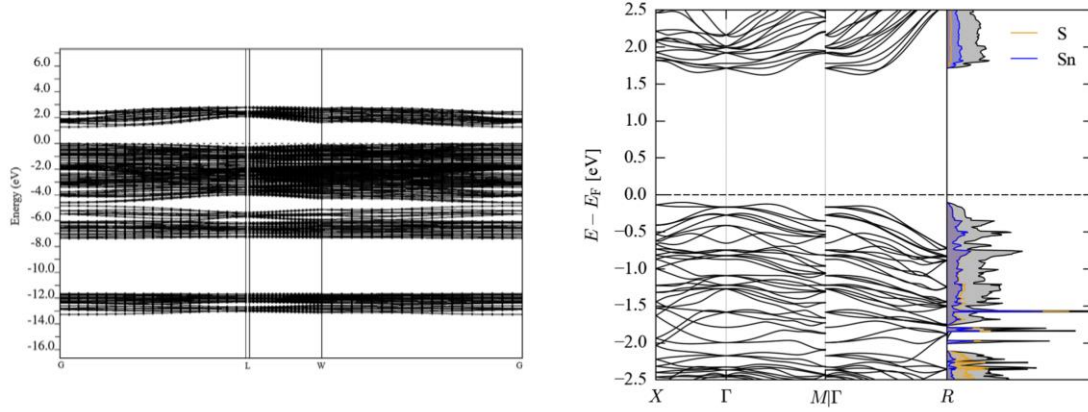


Figure 1.6 Calculated band Structure of π -SnS by two research groups: a) reproduced from Abutbul et al. [16] and b) reproduced from Skelton et al. [25].

1.5.2 Experimental optoelectronic properties

The optical and electrical properties of bulk single crystal SnS has been studied since early 20th century and again well-reviewed in Banai et al. [31].²⁵ Albers et al.[1] seems the most cited early authors that have done comprehensive characterization of SnS. According to their work and a few others as reviewed in Banai, SnS is an indirect bandgap material with $E_g \sim 1.1$ eV; the resistivity of single crystal SnS has shown orders of magnitude variation at room temperature, from less than $0.1 \Omega \cdot \text{cm}$ to a few $10 \Omega \cdot \text{cm}$; the hole mobility is on the order of $10 - 100 \text{ cm}^2/\text{V} \cdot \text{s}$, and the carrier concentration of the order of $10^{17} - 10^{18} \text{ cm}^{-3}$. The out of plane carrier effective mass and resistivity are roughly 5 times the in-plane values. It has also been seen that the hole mobility decreases with temperature, while concentration increases, agreeing with the theoretical predictions for a semiconductor.

²⁵ The review by Banai et al. also covered reports of direct bandgap characterized by ellipsometry and photoluminescence.

The experimental values of bandgap and electrical properties vary even more for thin films, especially when we consider the difficulties in composition and phase control. Both direct and indirect bandgap has been reported for thin film SnS, ranging from 0.98 eV to 2.3 eV. As a general observation, the average direct bandgap values are higher than the indirect ones, and bandgap decreases with increases in thickness and temperature, which has been explained mostly by the increase in grain size. The refractive index (n_{inf}) has been reported in the range 2 – 6 with 3 – 3.5 as a more common value. The range for resistivity is $10 - 10^6 \Omega \cdot \text{cm}$, which is much higher than the bulk value. The carrier concentration is on the order of $10^{14} - 10^{17} \text{ cm}^{-3}$, and mobility on the order of $1-10 \text{ cm}^2/\text{V} \cdot \text{s}$ with a few exceptions when films are epitaxially grown. The dielectric property of thin films was reported by a few groups to be $\epsilon = 12 - 13$, lower than the bulk value of 19.5 reported in [1].

Note that in most works, bandgap was measured by a UV-vis setup. Tauc plots are then constructed, where absorption in the form of $(\alpha h\nu)^n$ is plotted against photon energy to extrapolate bandgap from the region with linear behavior. Depending on the type of optical transition, the model that results in the best linear extrapolation is $n = 1/2$ for indirect allowed bandgap, $n = 3/2$ for direct forbidden bandgap, and $n = 2$ for direct allowed bandgap. Often, it is from looking at which model gives the best linear fit alone that one decides what type of bandgap the material has and the bandgap value. However, in practice sometimes the linear relationship is not very clear, and the model is selected, and the type of bandgap is concluded without sufficient justification. Other problems associated with SnS thin films are phase purity, thickness and crystallite size and stress-dependent band-modification, and even possible non-ideal optical properties of the substrate.

1.6 SnS solar cells and the approach of this thesis

Tin monosulfide (SnS) has demonstrated strong potential as a solar cell absorber due to its strong light absorption and simple binary system with only earth-abundant elements. As discussed in the previous section, the anisotropy of the thermodynamically stable α -SnS gives rise to strongly anisotropic electrical and optical properties, where the electrical conductivity and Hall mobility in-plane are five to six times higher than the out-of-plane values. Therefore, the orientation of the SnS thin film is important in solar cell fabrication and a SnS double layer perpendicularly aligned to the substrate such as in the (101) or (002) directions would favor carrier transport across the absorber, so that electrons and holes can be efficiently collected.

Solar cells based on α -SnS have reached efficiency up to 4.4% (certified) [29] or 5.2% (uncertified, this work) using SnS deposited by ALD as the p-type absorber and nitrogen doped Zn(O,S) as the n-type buffer layer. Thermally-evaporated SnS solar cells have reached efficiency of 3.9% using the same stack structure.[30] Recent progress in obtaining pure and large grain SnS has shown further potential for a higher efficiency cell due to improved carrier lifetime caused by reduced impurity and grain boundary defects.[87] Solar cells made with the cubic SnS thin film by chemical bath deposition have reached an efficiency of 1.28%. [18] Reviews by Banai et al. [31] and Di Mare et al. [32] cover pretty much all the SnS solar cells reported in literature so far. In this section I would like to focus on the challenges and outline the approaches taken in this work at address some of the challenges.

As discussed earlier, SnS is itself a challenging material to work with. First, pure and stoichiometric SnS films are difficult to obtain experimentally, but intrinsic defects that are detrimental to solar cell form easily. The available measurements on the carrier lifetime and diffusion length show that these properties of SnS are extremely poor. In fact, they can hardly be

measured using conventional methods such as time-resolved photoluminescence (TRPL) used for other solar cells, and measurement using terahertz spectroscopy shows a lifetime of the order of 100 ps, which is consistent with the estimation from the internal quantum efficiency (IQE) measured on a working cell. [88] The low carrier lifetime is likely to be caused by the high concentration of mid-gap defects that are recombination centers, leading to inefficient carrier collection and photo-voltage generation. However, we have not been able to reduce the defect sufficiently despite some extensive efforts in annealing by Hartman et al. where the loss of material put an upper limit on the processing temperature that might be too low to anneal out the defects.[80] Therefore, alternative ways of reducing SnS defects and improving the minority carrier lifetime are essential. To achieve this goal, it is essential to improve the deposition process and our understanding of the SnS formation mechanism, which will be addressed in Chapter 2 of this thesis.

Second, the studies on the crystal structures of SnS are not yet conclusive. The α -SnS has anisotropic properties and certain orientations are better than others for the solar cell. But no comprehensive work can be found on the orientations of SnS, and the sporadic results in literature sometimes seem inconsistent. A metastable cubic phase has long been observed alongside the stable α -SnS, but the inconsistencies in the literature might be only recently resolved by the proposal of a 64-atoms unit cell cubic π -SnS. The understanding of this phase is awfully limited, yet the available results show that it might harbor the potential for being a solar cell absorber. Besides, this cubic SnS has isotropic properties, and can avoid the orientation problem to some degree. Therefore, to it is necessary to conduct a systematic study of the SnS crystal structures and orientations to establish better controls over the material microstructure and subsequent optoelectronic properties, which will be addressed in Chapter 3 of this thesis.

Last, it is challenging to develop a solar cell even if we have a good absorber. The other layers and interfaces, such as the back contact, the n-type buffer layer, and the anti-reflection coating (ARC), are all important in making a good solar cell. Chapter 4 will address those issues in the device stack in connection to the work in Chapter 2 and 3 and conclude this thesis with future research directions.

2 Chapter 2 Atomic layer deposition and mechanistic studies of SnS

Abstract

This chapter discusses ALD growth behavior and mechanisms of SnS using a new and highly reactive liquid tin (II) precursor, bis(*N*, *N'*-diisopropylformamidinato)tin(II). Pure and stoichiometric SnS films can be obtained using this precursor and H₂S in the range of 65 – 180 °C. The reaction is surface-saturated and self-limiting, but the growth rate decreases with temperature. Mechanistic studies using a quartz crystal microbalance suggest that, at lower temperatures, it is more likely that both ligands of the Sn precursor molecule react with the surface thiol groups via ligand-exchange, forming a “Sn-bridge” upon the Sn-precursor exposure step, which explains the higher-than-expected growth rate predicted by steric hindrance of the ligands under the assumption of a typical layer-by-layer growth mechanism of ALD. Solar cells fabricated using SnS films deposited using this new precursor show comparable cell efficiency and improved device yield when compared against previous record solar cells deposited using bis(*N*, *N'*-diisopropylacetamidinato)tin(II).

2.1 Introduction

Tin(II) precursors for atomic layer deposition (ALD) and chemical vapor deposition (CVD) have attracted increasing attention due to their applications in making transparent conducting oxides (TCOs), such as tin dioxide (SnO₂) and zinc tin oxide (ZTO), [89-94] and solar cell absorbers, such as tin monosulfide (SnS). [23, 29, 51, 52, 55, 56, 95, 96] Compared to

the number of reports on and commercially available tin (IV) precursors used to make TCOs, relatively few reports are found on tin(II) precursors, [92] despite its versatility to make compounds of all chemical states and of both oxides and sulfides. Among the reported tin(II) precursors, only *N, N'*-di-*t*-butyl-2, 3-diamidobutanetin(II) and bis(*N, N'*-diisopropylacetamidinato)tin(II) have been reported to afford SnS as a light absorber for solar cells, with highest efficiencies of 2.9% and 4.4% respectively. [29, 52, 96]

The structural and electrical properties of SnS depend closely on the types of ALD precursors, each of which is suitable for a limited range of growth conditions such as substrate temperature, precursor dosage, and precursor exposure time. It has been reported that surface chemistry changes as growth temperature changes, [51, 97, 98] and that morphology and preferred orientation of the polycrystalline SnS films depend on precursors, growth temperature, type of substrates, and film thickness. [23, 52, 56] In addition, many currently available tin(II) precursors are solid at room temperature as well as at their respective vaporization temperatures in an ALD system. However, liquid precursors are in general preferred, especially in an industrial setting. First, it is easier to maintain a constant vapor pressure using a liquid precursor due to the constant surface area, contrary to a solid crystalline precursor where the crystallites can change in size and shape as it sublimes. Second, a liquid precursor will reduce the chance for particles to be delivered into the deposition chamber by the carrier gas. Third, it is easier to maintain a system with liquid precursor because, unlike solid ones, the (accidental) condensation of precursor is less likely to lead to serious clogging of the system. Therefore, development of new tin(II) precursors can improve precursor delivery and extend the range of growth conditions for SnS so that its properties can be further studied and optimized for solar cells.

In this chapter, we deposited SnS using bis(*N*, *N'*-diisopropylformamidinato)tin(II) as the Sn precursor, referred to as Sn(F-amd)₂. It is a liquid tin(II) precursor²⁶ at room temperature and exhibits excellent volatility (higher vapor pressure and evaporation rate at the same temperature) and thermal stability. We report an atypical ALD window, as well as a study of the surface reaction mechanism using a quartz crystal microbalance (QCM). We also demonstrate its utility in making device-quality SnS by ALD at low deposition temperatures, where film conformity and device yield were noticeably improved.

2.2 Experimental

The Sn(F-amd)₂ precursor was developed and synthesized by Dr. Sang Bok Kim. Thermogravimetric analysis (TGA) was used by Dr. Kim to investigate the volatility and thermal stability of this new precursor, along with the previously reported *N*, *N'*-di-*t*-butyl-2, 3-diamidobutanetin(II) and bis(*N*, *N'*-diisopropylacetamidinato)tin(II), referred to here as cyclic-Sn and Sn(A-amd)₂, respectively.

SnS was deposited by ALD in a custom-built hot-wall system using in-house synthesized Sn(F-amd)₂ and H₂S (Airgas, 4% H₂S in N₂) as tin and sulfur precursors. Each ALD cycle consisted Sn(F-amd)₂ dosing → exposure → N₂ purging → vacuum → H₂S dosing → exposure → N₂ purging → vacuum. Nitrogen was used as carrier gas to facilitate transport of the Sn precursor. Each dose of Sn(F-amd)₂ delivers 10 torr and each dose of H₂S delivers 3 torr of total pressure to the reactor.²⁷ First, surface saturation was examined with respect to precursor

²⁶ Other common liquid tin precursors include Sn(acac)₂ (Mp ca. -20 °C), and TDMASn.

²⁷ The vapor pressure of Sn(F-amd)₂ without carrier gas was measured using a Pirani gauge, which is not the best for measuring pressures other than inert gas. The vapor pressure shall be measured with a capacitance manometer in the future. The partial pressure of H₂S can be calculated from its concentration as 120 mtorr per dose.

exposure by varying the vaporization temperature and number of doses. The purging time was also varied to examine whether the excess precursor and by-product are completely removed. ALD of SnS was then studied at a temperature range of 65 °C – 200 °C, using 1 dose of each precursor, 3 s of exposure time, 10 s of purging time and 10 s vacuum time. The Sn(F-amd)₂ precursor was kept in an oven held at 65 °C and the H₂S tank was kept at room temperature. Films were deposited on flat silicon thermal oxide substrates, as well as on silicon trenches with an aspect ratio of 25:1 obtained by reactive ion etching to confirm step coverage.

To understand the surface reaction mechanism at different deposition temperatures, the mass change during one cycle of ALD was investigated using an in-situ QCM at three different temperatures. Surface chemistry was identified by observing the ratio $\Delta m_2/\Delta m_1$, where Δm_1 is the mass change (usually positive) resulting from the surface reaction after the exposure of Sn(F-amd)₂, and Δm_2 is the mass change (usually negative) resulting from the surface reaction after the exposure of H₂S. Molybdenum (500 nm) was sputtered onto the gold covered QCM surface prior to the experiment to simulate real growth conditions for a solar cell.²⁸ The experiment was done on the same crystal in the order of 80 °C, 160 °C, and 120 °C and a pulse sequence of Sn(F-amd)₂ dosing (1 s) → exposure (3 s) → N₂ purging (30 s) → vacuum (10 s) → H₂S dosing (1 s) → exposure (3 s) → N₂ purging (30 s)²⁹ → vacuum (10 s) was used. Then the exposure time was varied between 10 s to 60 s and the purging time between 30 s and 90 s study their respective effect. Note that due to the high surface roughness of the quartz crystal and its sensitivity to

²⁸ The SnS growth rate and morphology are roughly the same on molybdenum and on thermal oxide substrates, but meaningfully different on gold.

²⁹ Note that a longer purging time of 30 s was used in the QCM experiments compared to most of the thicker films depositions, in other depositions to guarantee that physisorbed precursors and surface reaction by-products should be completely removed during purging period.

temperature, the mass readings of QCM (in ng/cm²) were calibrated against the growth rate of SnS on thermal oxide substrates at their respective temperatures. Because this calibration is a linear scaling, it will not impact the ratio of $\Delta m_2/\Delta m_1$ nor the subsequent conclusions based on it.

The morphology of the films was examined by field emission scanning electron microscopy (FESEM, Supra55VP). X-ray Photoelectron Spectroscopy (XPS, Thermo Scientific K-Alpha) was used to characterize the composition of the SnS film. Argon ion sputtering of 30 s at 500 eV was used to clean the surface oxide or carbon prior to XPS composition measurements. Survey scans were performed on films grown at various temperatures, and the spectra were analyzed using the Thermo Advantage software to obtain compositions.

Solar cell devices were fabricated using 720 nm of SnS films deposited at 120 °C by Sn(F-amd)₂. The films were annealed in H₂S³⁰ for 1 hour after deposition and subjected to 24 hours of ambient exposure for passivation by a thin layer of SnO_x. Nitrogen doped Zn(O,S) was then deposited as the buffer layer. A detailed description of the solar cell structure and the fabrication procedures can be found in a previous paper.[29] On a 1 in² sample, 12 devices were fabricated with an active area of 0.24 cm² each. The current-voltage (J-V) characteristics was measured using Agilent 4156C and Keithley 2400 semiconductor characterization systems under 100 mW/cm² AM 1.5G illumination. The key performance characteristics were then compared to those of the devices fabricated using SnS films deposited by Sn(A-amd)₂ of the same thickness at 200 °C, which was previously reported as the optimal deposition temperature for that precursor. [28, 29]

³⁰ Both 100% and 4% H₂S were used. No difference was found in morphology, crystal structure, or device performance.

2.3 Result and Discussion

2.3.1 Precursor Characterization

This section (2.3.1) is adapted from an unpublished text by Dr. Sang Bok Kim, except for the last paragraph, to provide background information on this ALD precursor.

A colorless liquid tin(II) precursor was obtained with excellent volatility and thermal stability. Thermogravimetric analysis (TGA) shows that under a linear temperature ramp (sample 14 mg, 10 °C/min), single-step weight loss was observed in the temperature range of 70 °C – 200 °C. With a larger sample (81 mg) and faster heating rate (20 °C/min), the weight loss window was elevated as expected, and single-step weight loss occurred in the range of 150 °C – 270 °C, as can be seen in figure 2.1a. It was shown that $\text{Sn}(\text{F-amd})_2$ can vaporize without decomposition in the above temperature ranges on the time scale of the TGA experiment, indicating excellent thermal stability to at least 260 °C, which meets one of the requirements for an ALD precursor, thermal stability during mass transport to the substrate surface at the film growth temperature.

Figure 2.1b shows the slopes of the logarithms of evaporation rate vs. temperature for the three precursors obtained in isothermal TGA experiments. Evaporation rates of $\text{Sn}(\text{F-amd})_2$ lies in the middle of cyclic-Sn and $\text{Sn}(\text{A-amd})_2$, where 40 °C – 45 °C and 90 °C – 95 °C as source temperatures for ALD have been used respectively as reported in the literature.[29, 99] The source temperature for $\text{Sn}(\text{F-amd})_2$ for this work, 65 °C – 70 °C, lies in between cyclic-Sn and $\text{Sn}(\text{A-amd})_2$, with a temperature difference of 25 °C with each, and roughly matches the temperature difference at a constant evaporation rate. At an elevated temperature of 100 °C, both $\text{Sn}(\text{F-amd})_2$ and $\text{Sn}(\text{A-amd})_2$ (the amidinate complexes) are liquids, but the evaporation rate of $\text{Sn}(\text{F-amd})_2$ was found to be 4.4 times higher than that of $\text{Sn}(\text{A-amd})_2$. By replacing the $-\text{CH}_3$

group in the acetamidinate with the -H in formamidinate, volatility is significantly improved by and the enthalpy of vaporization is lowered as shown by the slopes of the logarithms of evaporation rate vs. inverse temperature in Figure 2.1b.

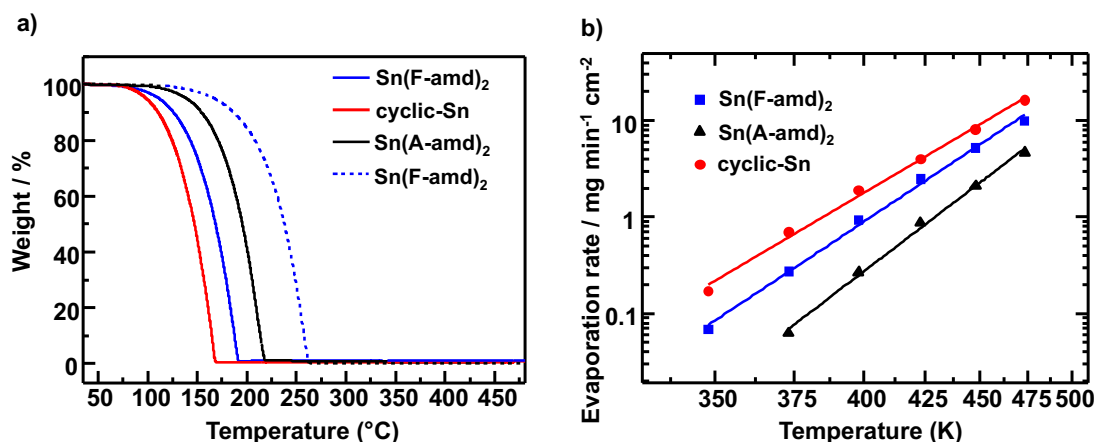


Figure 2.1 Thermogravimetric Analysis; a) TGA curves (ramp from RT to 500 °C) of Sn(F-amd)₂ (black solid line, 14 mg, 10 °C/min), cyclic-Sn (red solid line, 14 mg, 10 °C/min), Sn(A-amd)₂ (blue solid line, 14 mg, 10 °C/min), and Sn(F-amd)₂ (black dashed line, 81 mg, 20 °C/min), b) plot of evaporation rates (mg/min·cm², log. scale) vs. temperature (Kelvin, reciprocal scale). (This figure is generated by Dr. Sang Bok Kim)

Thermal stability was further demonstrated when minimal decomposition was observed after being used in the ALD system held at vaporization temperature for 6 months, where carbon free SnS films were obtained at constant growth rate until the precursor was nearly-completely consumed with just traces of a grey-white solid residue left on the wall of the bubbler.³¹

2.3.2 ALD growth behavior

Figure 2.2 shows surface-saturation self-limiting ALD behavior. The source temperature of 65 °C is sufficient to generate enough vapor pressure as shown in figure 2.2a when deposition

³¹ We suspect this residue to be a mixture of tin-oxides and tin-sulfides caused by leakage.

was conducted using an intermediate substrate temperature of 120 °C. Figure 2.2b and figure 2.2c show that the surface is saturated with one dose of each precursor at different temperatures. Figure 2.2d confirms that the excess precursor and by-product can be completely removed by the 10s purging and 10s vacuum after each precursor dose regardless of the temperature. These results show surface-saturated and self-limiting ALD reaction with no or minimal CVD components at all temperatures, which establishes the basis for the mechanism study in the next section.

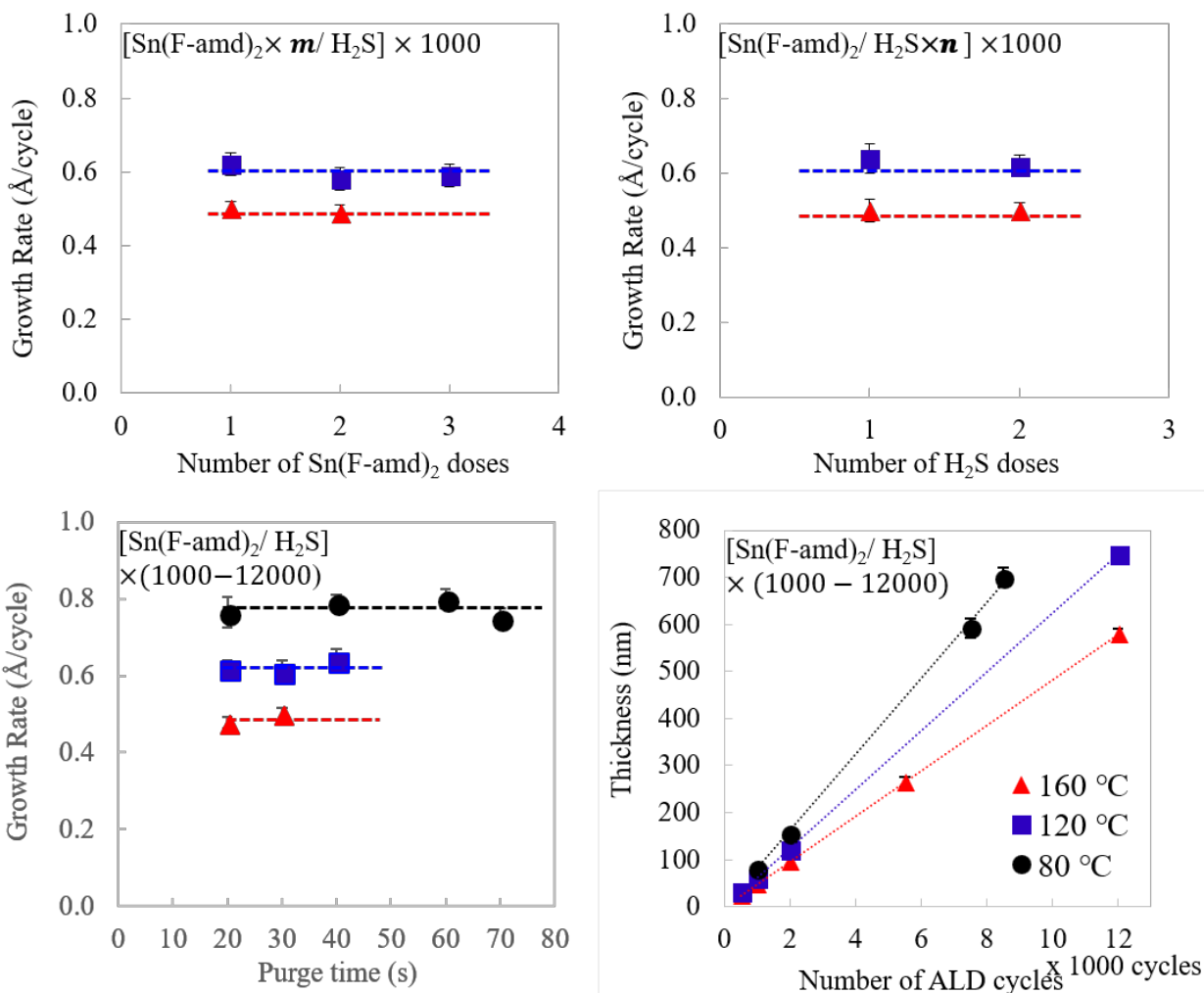


Figure 2.2 Data showing that film growth rate at a constant temperature approaches a constant value as source temperature, precursor dosage, or purge/vacuum time increases. (a) Growth rate of SnS films using different source temperatures. (b) Growth rate of SnS films using different doses of Sn(F-amd)₂ and fixed 1 doses of H₂S. (c) Growth rate of SnS films using different doses of H₂S and fixed 1 doses of Sn(F-amd)₂. (d) Growth rate of SnS with different amounts of vacuum+purging time to remove the excess precursor and by-product. The error bar on each point is from multiple measurements of at least two samples in the same run of deposition.

The ALD window of SnS using Sn(F-amd)₂ and H₂S was found to be 0.86 Å/cycle – 0.31 Å/cycle in the temperature range of 65 °C – 200 °C as presented in figure 2.3, revealing a trend of decreasing growth rate with increasing temperature, which, though atypical for an ideal ALD system, has been reported for ALD of SnS using other Sn precursors such as Sn(dmamp)₂ and

TDMA₂Sn,[53, 55] although relatively constant growth rate has been reported using Sn(acac)₂ and Sn(A-*amd*)₂. [23, 52]

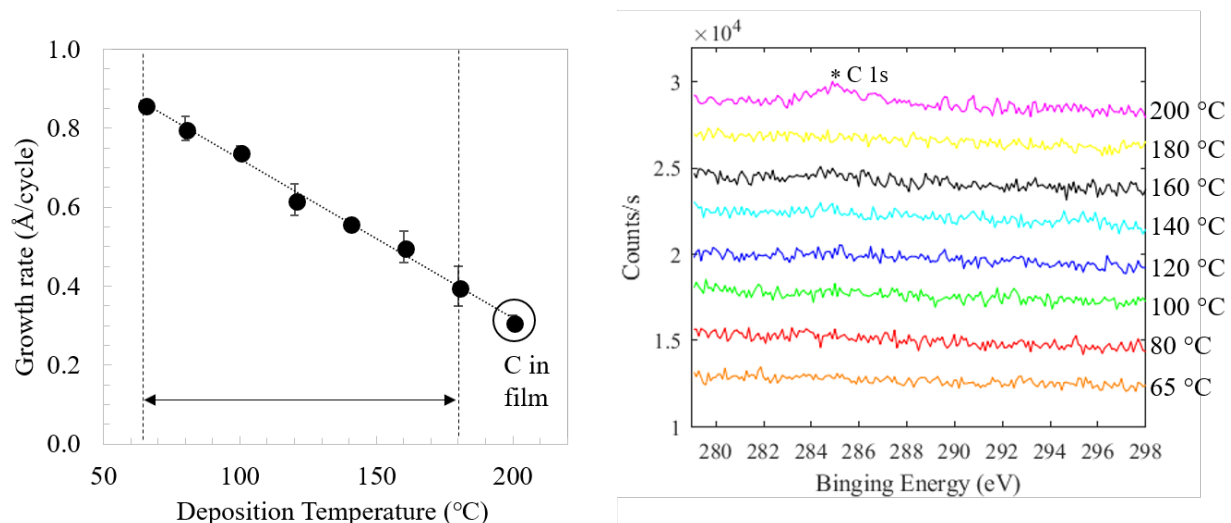


Figure 2.3 Temperature dependence of growth rate. (a) Growth rate of SnS as function of substrate temperature between 65 °C and 200 °C. (b) Film thickness as a function of number of ALD cycles at three different temperatures.

2.3.3 ALD reaction mechanism

The expected surface chemistry as in a typical ALD procedure of SnS is presented in figure 2.4 for our ALD reaction. Upon dosing of Sn(F-*amd*)₂, an S-Sn bond is formed and the -SH terminated surface is converted to a ligand terminated surface; the following dose of H₂S forms another S-Sn bond and converts the surface back to -SH termination. Ideally, this layer-by-layer process is stoichiometric and should not depend on temperature, and the growth rate can be as high as 5.6 Å/cycle for these precursors, equivalent to a mass gain of 290 ng/cm² per ALD cycle, if one monolayer per cycle is realized, for example, along the b-axis of α-SnS. This value is much higher than the actual growth rate observed.

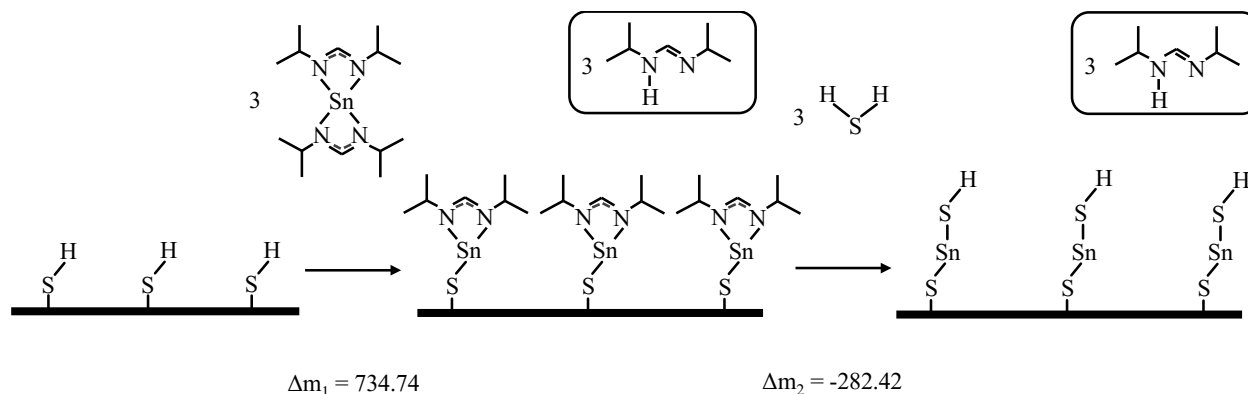


Figure 2.4 Schematics of a typical ALD procedure for SnS using $\text{Sn}(\text{F-amd})_2$ and H_2S as precursors. The mass change (in unit of molecular weight) during each half-reaction is labeled as Δm_1 for Sn exposure and Δm_2 for S exposure. The boxed molecules indicate reaction by-products, which are to be removed.

The growth rate in the ALD process is in reality determined by one of two mechanisms: surface saturation via the number of reactive surface sites, or surface saturation via the steric hindrance of the ligands, as illustrated by Puurunen [97].³² A theoretical growth rate can be calculated in the case of each surface saturation condition, if the ligand size (r_L) or the equilibrium concentration of the reactive surface sites ($c_{(S)H}^{eq}$) is known. The maximum growth rate should be the lower value of the two.

If our SnS growth rate is limited by surface saturation caused by the number of reactive surface sites, the theoretical maximum growth rate can be calculated from surface -SH site concentration. In the α -SnS crystal, the atomic area concentration of Sn or S is approximately 5.81 nm^{-2} in the $\{010\}$ plane (densest packed plane of all atoms with a 11.62 nm^{-2} of atomic area concentration of Sn+S) and 6.72 nm^{-2} in the $\{021\}$ plane (densest pack plane of the individual

³² Note that growth rate can also be limited by surface saturation and reactivity of the precursors, which is less likely to be a concern here, given that our precursors are highly volatile and reactive, and surface saturation has been shown to be achieved.

element).³³ This corresponds to a maximum growth rate of 2.8 Å/cycle in the (010) direction and 3.24 Å/cycle in the (021) direction.

Given our actual growth rate of **0.86 Å/cycle – 0.31 Å/cycle** in the temperature range of 65 °C – 200 °C, and the **3.24 Å/cycle** growth rate at 6.72 nm⁻² S (or Sn) atomic concentration in the (021) direction, we can infer our thiol surface concentration to be **1.78 nm⁻² – 0.64 nm⁻²** with a temperature dependence of -0.84 nm⁻² · (100 °C)⁻¹ between 65 °C – 200 °C, which is within one order of magnitude of some literature values reported for surface hydroxyl groups³⁴ [97] or alkyl-thiol groups. [100]

In the steric hindrance scenario, we can calculate the maximum growth rate if the formamidinate ligand can be approximated with a spherical shape with a radius of $r_L = 0.42$ nm based on the crystallographic data for the dimeric calcium(II) formamidinate. [101] Thus, each ligand occupies an area of $a_L = 2\sqrt{3} r_L^2 = 0.61$ nm² under close packing and theoretical upper limit of surface ligand concentration is $c_L^{maxthr} = \frac{1}{a_L} = 1.64$ nm⁻². We should also note that close packing of ligand is often not achieved, and according to Puurunen, the maximum realistic ligand coverage is $\theta_{max} = 0.7$ and is independent of temperature, which lowers the upper limit to $c_L^{max} = 1.15$ nm⁻². Assuming each ligand is attached to one Sn atom as shown in figure 2.4, the Sn atom

³³ Sn or S atom area concentration in the {010} plane is 1 nm²/(a*c) = 5.81 nm⁻², so the total atomic area concentration is 11.62 nm⁻². From the geometry, it is reasonable to assume that one unit cell of SnS can be obtained with 4 cycles of ALD growth of the {010} plane and 2 cycles of the {021} plane, and we know that the growth rate of the {010} plane is b/4 = 2.8 Å/cycle. Thus, the growth rate of the {021} plane is $\Delta h = 2 * 2.8$ Å/cycle *

$\sin\left(\arctan\left(\frac{c}{b*0.5}\right)\right) = 3.24$ Å/cycle. The Sn or S atom area concentration in the {021} plane can be calculated to be $\frac{11.62 \text{ nm}^{-2}}{5.6 \text{ Å/cycle}} * 3.24 \frac{\text{Å}}{\text{cycle}} = 6.72 \text{ nm}^{-2}$.

³⁴ Surface concentration of hydroxyl group decreases linearly from 10 sites/nm² to 0 from 0 °C to 1000°C.

density would also be **1.15 nm⁻²**. Thus, the maximum growth rate is $\Delta h_{\text{SnS}}^{\text{max}} = 0.55 \text{ \AA/cycle}$, which is equivalent to less than one-fifth of a monolayer of SnS growth per cycle.

Based on the calculation above, the maximum theoretical growth rate for our SnS should be 0.55 Å/cycle and independent of temperature, where saturation of the surface is defined by steric hindrance of the formamidinate ligand. Yet, the real surface –SH site concentration could be lower than our assumed value in the model, in which case the growth rate would be lower than 0.55 Å/cycle and decrease with temperature. We may use the surface sites defined surface saturation mechanism to explain the decreasing growth rate at temperatures higher than 140°C, although that seems unlikely to be the only explanation, because the surface concentrations of the –SH groups would need to be roughly one-tenth of that in the assumptions in [97, 100] as discussed earlier. Also, we cannot yet explain the higher than 0.55 Å/cycle growth rate at lower temperatures.

Therefore, we propose a modification to the typical mechanism in figure 2.5, allowing both ligands of the Sn(F-amd)₂ molecule react with the surface –SH sites, forming a “Sn-bridge” as shown in figure 2.6a. This lets some of the –SH sites previously blocked by the large ligands to be again accessible, thus increasing the Sn atom concentration and increasing the growth rate beyond the steric hindrance limit. It would not be unexpected that the free energy of Sn-bridge formation is negative, where entropy is increased by the gaseous by-product; thus, the reaction rate would increase with temperature and we should expect more Sn-bridges at higher temperatures, if the surface thiol density stays constant.

During the second half-reaction, the H₂S molecules can dissociatively (or associatively) react with the Sn-bridges as shown in figure 2.5b, so that the surface –SH concentration is recovered, and a sustainable growth rate can be achieved. However, this process likely decreases

the entropy, and we would thus expect less H_2S to react with the Sn-bridge as temperature increases, which could be the reason for the decreasing surface thiol concentration and decreasing growth rate with increasing temperature. Likewise, during the S exposure step, S-bridges may also occur as in the dot-boxed part of figure 2.5b, and Sn precursor molecules can associate or dissociate in the next step, although less likely due to steric reasons.

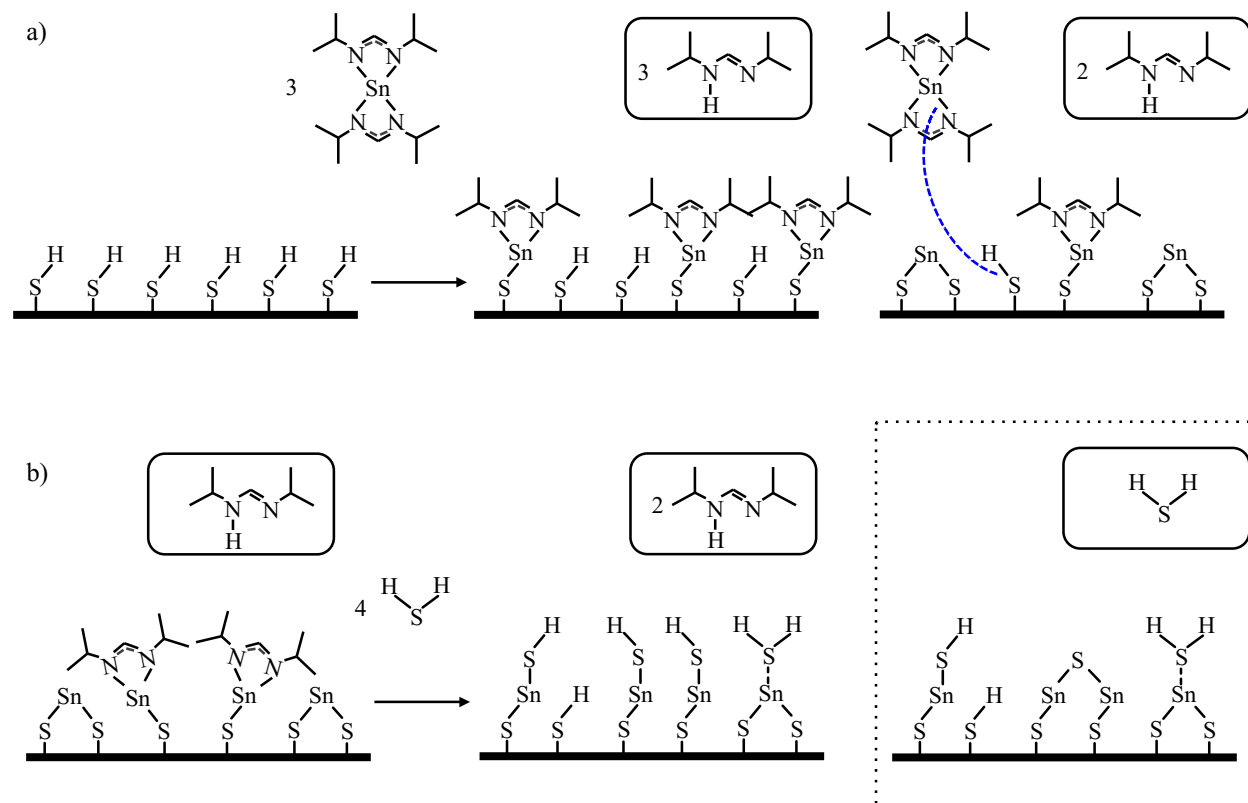


Figure 2.5 Schematics of the modified ALD procedure for SnS using $\text{Sn}(\text{F-amd})_2$ and H_2S as precursors with “Sn-bridges” and “S-bridges” formation. (a) The half reaction during Sn-exposure, (b) The half reaction during S-exposure with H_2S dissociation and association mechanism. The boxed molecules indicate reaction product to be removed by purging.

In connection with the Sn-bridge formation as discussed in the previous paragraph, we cannot conclude whether more or less Sn-bridges form as temperature increases, because while thermodynamics may favor it at high temperatures, the decreased density of surface thiol groups would oppose it. We are only more certain that a larger number of Sn-bridges would react with

H₂S (“opens up”) at lower temperatures, which could contribute to the higher growth rate. From the steric hindrance perspective, we might expect that as temperature decreases, more Sn-bridges form and more space for additional Sn precursor molecules are revealed on the surface, thus contributing to the higher-than-steric-hindrance-defined growth rate. Due to the multiple factors (thermodynamic and steric effects playing during both half reactions) discussed above, we do not expect the growth rate to follow a simple Arrhenius relation.

As a quick summary, growth rate increases as temperature decreases, and can increase beyond the “theoretical maximum” determined by steric hindrance under the typical mechanism. Since we allow the double-ligand-exchange which forms Sn bridges and we know that growth rate does not change with exposure amount or purging time, we suggest that the reaction is ultimately limited by the surface thiol group concentration, but the fraction of Sn-bridge and the amount of surface ligand coverage may vary. As a side note, there could exist unreacted Sn-bridges or S-bridges, and even unreacted thiol groups as blocked by ligands. We speculate that they may disrupt the film continuity and be a potential source of defects.

We can test the above mechanistic hypothesis by measuring the ratio of mass changes upon the two half reactions, as denoted by $\frac{\Delta m_2}{\Delta m_1}$, at different temperatures. Depending on how many “Sn bridges” form and how many of them would subsequently react with H₂S, the ratio

$\frac{\Delta m_2}{\Delta m_1}$ can vary considerably. Under the typical scenario as shown in figure 2.5, the ratio

$(\frac{\Delta m_2}{\Delta m_1})_{typ} = \frac{-282.42}{734.74} = -0.38$. If all of the ligands react with the surface thiol groups (the surface

is completely terminated with Sn-bridges without any ligand) and all of them are chemically

reactive, we get the upper limit of the value of the ratio $(\frac{\Delta m_2}{\Delta m_1})_{max} = \frac{M_{H_2S}}{M_{Sn-2}} = \frac{32.06+2*1.008}{118.71-2*1.008} =$

+0.29 (assuming no “S-bridge” is formed). Generally speaking, the Sn-bridges cause the ratio

$\frac{\Delta m_2}{\Delta m_1}$ to increase while the S-bridges causes it to decrease. In addition, the more the non-reactive/terminal Sn-bridges and S-bridges, the lower the growth rate, due to reduced reactive surface sites.³⁵

Figure 2.6a presents the QCM measurement of mass change vs. time for SnS ALD at 80 °C, 120 °C, and 160 °C. We see that the mass gain is linear with time, with an initial lower growth rate at 80 °C due to nucleation. This incubation period only appears in the 80 °C film because it was grown on the Mo-coated surface and the other two films were grown atop the 80 °C film. It is observed that the raw QCM data deviates considerable from the true growth rate, perhaps due to the quartz crystal's uneven surface and sensitivity to temperature and pressure perturbations. The effect of temperature and pressure on QCM readings, as well as a cross-sectional image of a quartz crystal coated with SnS films can be found in Appendix C. Therefore, the mass values measured by QCM are calibrated against the true growth rate of the film, as shown in figure 2.2 and 2.3.³⁶

³⁵ Note that the growth rate observed both in QCM and in actual film growth (Figure 3d) stays constant versus the number of SnS cycles, which indicates that the reactive and non-reactive “Sn bridges” should be in equilibrium, and the number of reactive sites does not decrease with each cycle of ALD growth.

³⁶ To solve the mystery of the high growth rate and inconsistency between crystals, I deposited roughly 50nm of film and imaged its cross section under SEM. The quartz crystal has a very uneven surface with many cracks and grooves, which was covered uniformly with our SnS films. While it demonstrates excellent step coverage of our ALD process, the effective surface area could be several times higher than the value used in the data output as ng/cm² and is dependent on the individual crystal.

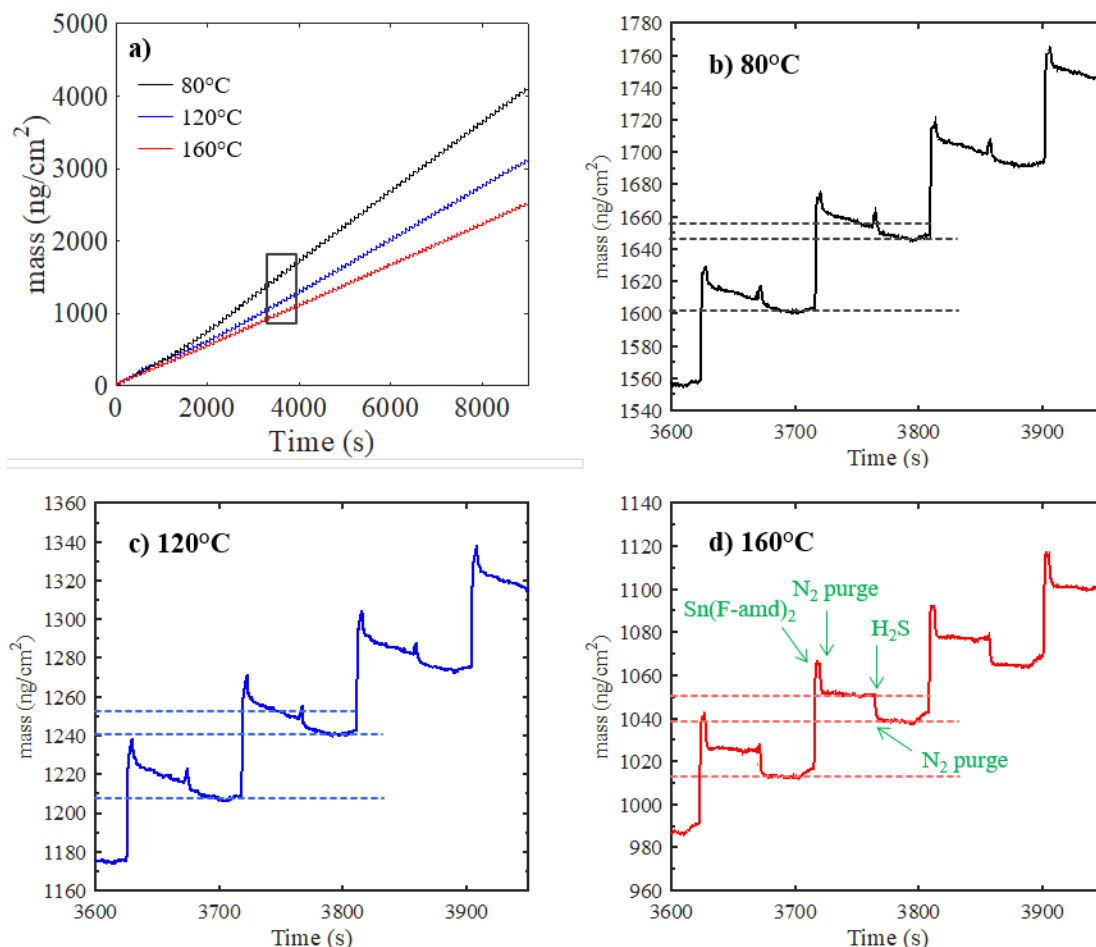


Figure 2.6 (a) QCM of mass change vs. time for 100 cycles of SnS ALD at three different temperatures. (b) (c) and (d) are zoomed in images of (a) on three ALD cycles at each temperature.

Figure 2.6b-d show the close-up images of three cycles of $\text{Sn(F-amd)}_2 / \text{H}_2\text{S}$ at the three temperatures and illustrate how the mass change Δm_1 and Δm_2 is obtained. Note that we observe an increase in mass at the end of the purging step, which is possibly due to pressure and temperature perturbation caused by the sudden shut off of purging gas and turning on of the vacuum pump prior to the precursor dose. Therefore, we use the value of mass at the end of the 30s purging to best approximate the equilibrium condition and estimate Δm_2 and Δm_1 . Table 1 summarizes the mass gain (Δm_1) and mass loss (Δm_2) and their ratio $\frac{\Delta m_2}{\Delta m_1}$ at different

temperatures. Each value is an averaged over 3 – 5 cycles in the middle of the 100 cycles. The ratio $\frac{\Delta m_2}{\Delta m_1}$ stays negative but decreases monotonically with temperature, approaching the value of -0.38 as calculated for the typical case in figure 2.4. This result would support our hypothesis that more Sn-bridges form at lower deposition temperatures in the ALD process; and at lower temperatures, the concentration of surface –SH is also higher, which leads to the high mass gain (Δm_1) upon the Sn exposure. In addition, as shown in figure 2.2, no change in growth rate was observed for films deposited using different exposure/trap or purge time, which should be able to rule out the possibility that the high growth rate is caused by insufficient removal of the excess precursor and subsequently more CVD reactions at lower temperature.

Table 2.1 The average mass gain (Δm_1) and mass loss (Δm_2) during the ALD of SnS at different temperatures.

Temperature (°C)	Δm_1 (ng/cm ²)	Δm_2 (ng/cm ²)	$\Delta m_2 / \Delta m_1$
160	38 ± 1	-12 ± 1	-0.32 ± 0.03
120	44 ± 1	-12 ± 1	-0.27 ± 0.03
80	54 ± 1	-10 ± 1	-0.19 ± 0.02

In addition, the effect of precursor exposure and purge time was also investigated. QCM results in table 2.2 show that the ratio $\frac{\Delta m_2}{\Delta m_1}$ decreases with both exposure and purge time, indicating that more Sn-bridges may form given more time for reaction, which may be caused by the ||–S–Sn–L further harvesting any highly mobile hydrogen on the surface.

Table 2.2 The average mass gain (Δm_1) and mass loss (Δm_2) during the ALD of SnS at 120°C using different exposure times for the Sn precursor with a fixed purge time of 60s, and using different purge times with a fixed exposure time of 10s.

Exposure time (s)	Δm_1 (ng/cm ²)	Δm_2 (ng/cm ²)	$\Delta m_2/\Delta m_1$	Purge time (s)	Δm_1 (ng/cm ²)	Δm_2 (ng/cm ²)	$\Delta m_2/\Delta m_1$
10	42 ± 1	-10 ± 1	-0.24 ± 0.03	30	43 ± 1	-11 ± 1	-0.26 ± 0.03
30	39 ± 1	-8 ± 1	-0.21 ± 0.03	60	42 ± 1	-10 ± 1	-0.24 ± 0.03
60	31 ± 1	-1 ± 1	-0.03 ± 0.03	90	39 ± 1	-7 ± 1	-0.18 ± 0.03

We should note that there are many possibilities for how and what types of bonds are formed in each half-reaction of ALD. The “Sn-bridge” mechanism proposed above is one that can explain the temperature dependence of the growth rate and is consistent with both our theoretical calculation and experimental observations.³⁷ In addition, the electronic and crystal structure of SnS can bring in additional complications to the ALD mechanism, because the (2+) charged Sn is bonded to four N of the two (1-) charged formamidinate ligands (each Sn–L is shared by one Sn and two N) in the Sn precursor, and each S is bonded to two H in the H₂S precursor. However, in the crystal, each Sn bonds to three S while its lone pair electrons points towards the space between the double layers as in the α -SnS, or points outwards from the pyramid basis structure as in the cubic π -SnS, [16, 19] and each S is also bonded to three Sn

³⁷ Wang et al., [unpublished] recently proposed another ALD mechanism of nickel sulfide using nickel-amidinate precursor and H₂S. Their work shows that the amidinate ligands might not be completely removed by the H₂S dose, but instead, were adsorbed to the –SH groups by acid-base attraction, as shown. This mechanism can also explain the trend of $\Delta m_2/\Delta m_1$ observed in the deposition of SnS, but it alone cannot explain the change in growth rate with temperature.

atoms. Thus, it is not a one-to-one conversion of the Sn–L bonds in the precursor to the Sn–S bonds in the crystal, which leads to more complication.

2.3.4 Composition and morphology

Pure SnS films were obtained at substrate temperatures from 65 °C up to 180 °C as shown in figure 2.7. Oxygen, carbon, and nitrogen contents were all below the detection limit of XPS within this temperature range. The SnS films were close to stoichiometric with a maximum of 1.5 at. % deviation where the Sn content appears to be slightly higher than S in most cases without any particular trend, which could be due to measurement accuracy as well as preferential sputtering for the more volatile S during the Ar ion sputtering process.

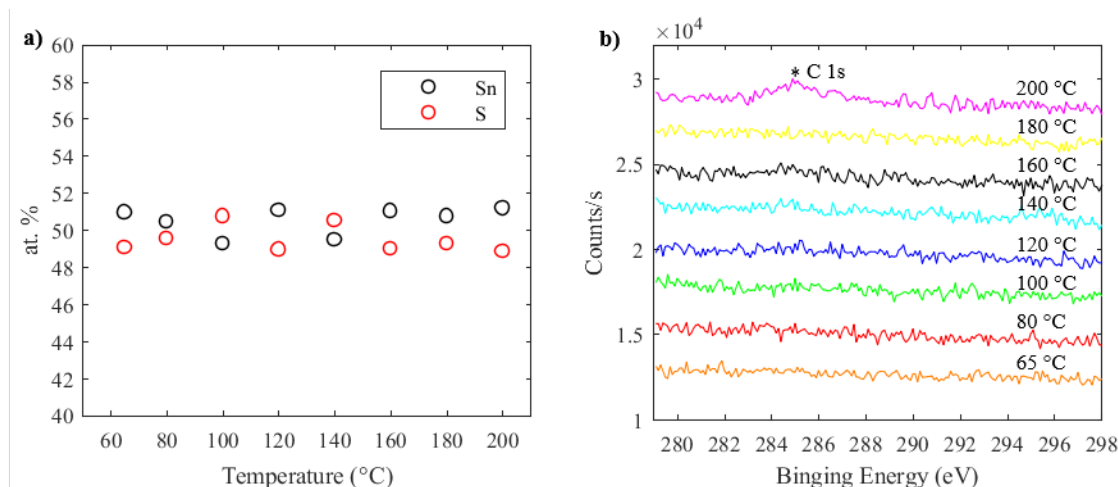


Figure 2.7 Composition of SnS films deposited at different temperatures. (a) Atomic % of Sn and S, (b) XPS scan of C 1s peak showing no carbon presence up to 180 °C. Data are taken after 30s of Ar sputtering to remove surface carbon and oxygen.

In the high-resolution XPS scan (figure 2.8), the Sn 3d_{5/2} peak can be observed at 486.05 ± 0.05 eV in all films, which agrees with literature values of Sn²⁺ in SnO and SnS. A small peak with 1 eV lower binding energy corresponds to the Sn⁰ peak, which is due to the reduction and

preferential sputtering of S, caused by Ar sputtering. An XPS study of the effect of Ar voltage can be seen in Appendix D.

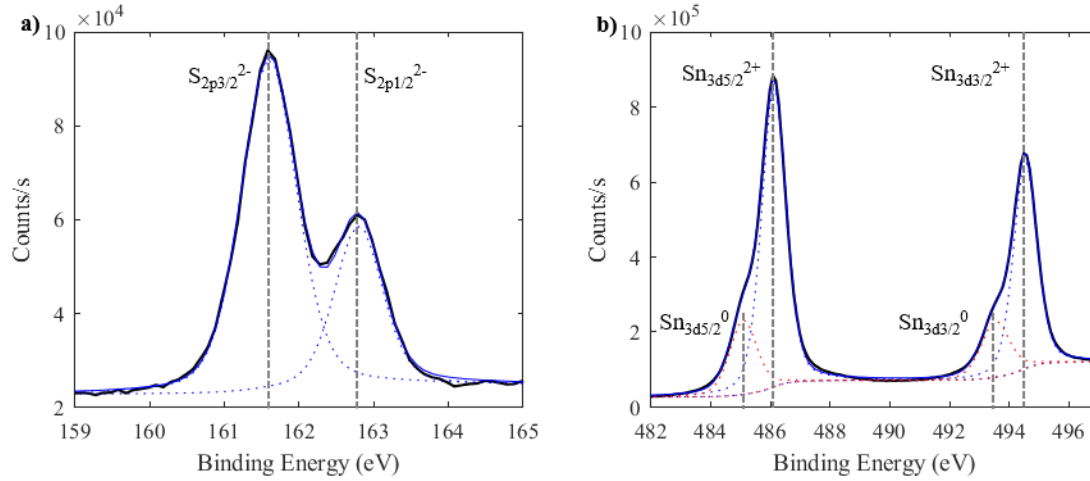


Figure 2.8 High Resolution XPS scan of (a) S and (b) Sn, after 120 s of Ar sputtering at 500eV to remove all surface carbon and oxygen.

Figure 2.9 and 2.10 show the SEM images of SnS film deposited at different temperatures on flat silicon thermal oxide substrates. We see that as temperature increases, both grain size and surface roughness increase, and the irregular granular grains gradually assumed rectangular-plate shape. The trench sample (figure 2.11) demonstrates that $Sn(F\text{-amd})_2$ is capable of complete and uniform coverage of high aspect ratio structures.

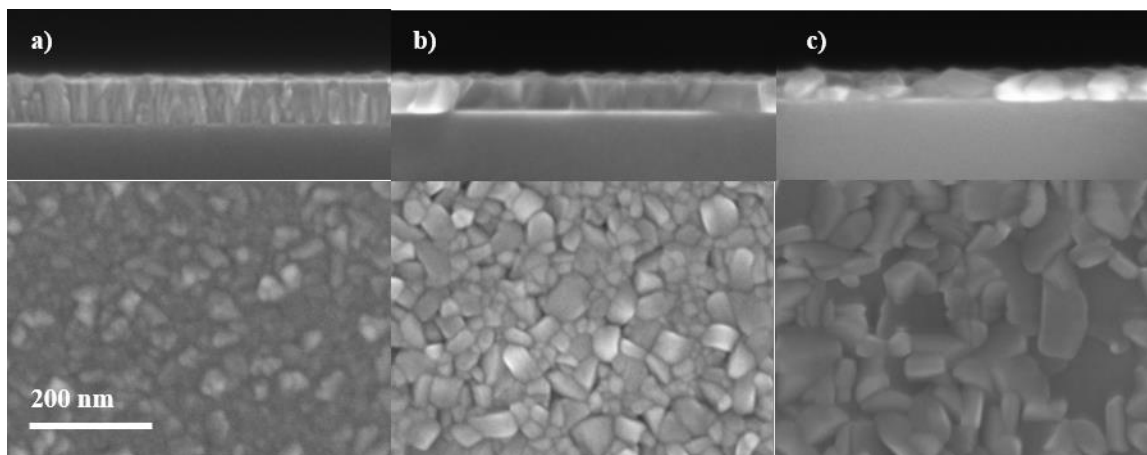


Figure 2.9 Top view and side view SEM images of 1000 cycles of SnS deposited at temperatures: (a) 80 °C (b) 120 °C, and (c) 160 °C.

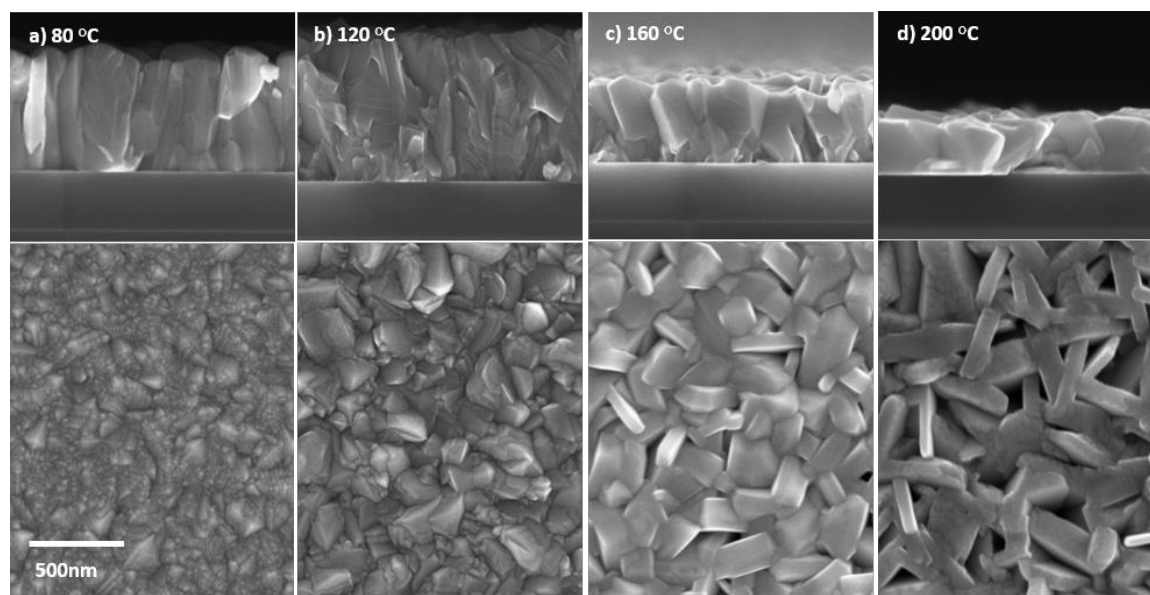


Figure 2.10 Top view and side view SEM images of thick SnS films deposited on thermal oxide substrate. (a) 7500 cycles at 80 °C (b) 12000 cycle as 120 °C, and (c) 9000 cycles at 160 °C, and 16000 cycles at 200 °C.

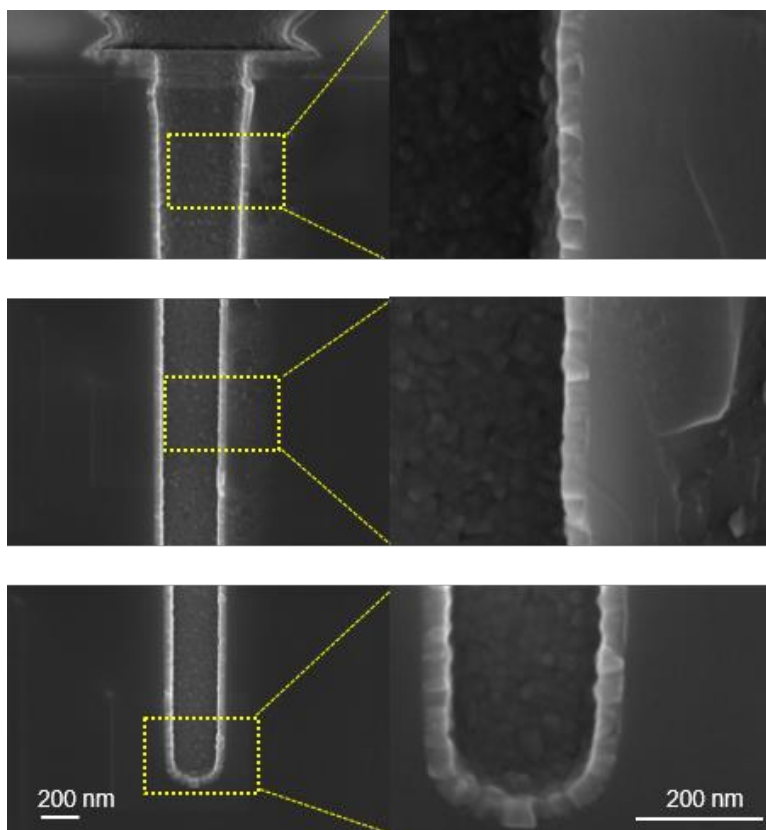


Figure 2.11 Cross-sectional images of a hole with aspect ratio of 25:1 covered by 750 cycles of SnS deposited at 120 °C at different positions.

2.3.5 Solar cell performances

Performance characteristics of devices using 700 nm of SnS films deposited from Sn(F-amd)₂ (12 cells) and Sn(A-amd)₂ (12 cells) are presented in Figure 2.12. The best cell using Sn(F-amd)₂ showed higher open-circuit voltage (V_{OC}) and short-circuit current (J_{SC}), but slightly lower fill factor than the best device using Sn(A-amd)₂, leading to similar efficiencies. However, it worth noting that the consistency of performance was significantly improved using Sn(F-amd)₂. The highly reactive Sn(F-amd)₂ enables high-quality SnS to be deposited at lower temperatures, which not only reduces processing temperature, but also leads to denser nucleation and a more conformal coverage, which persisted even after annealing during our solar cells fabrication.

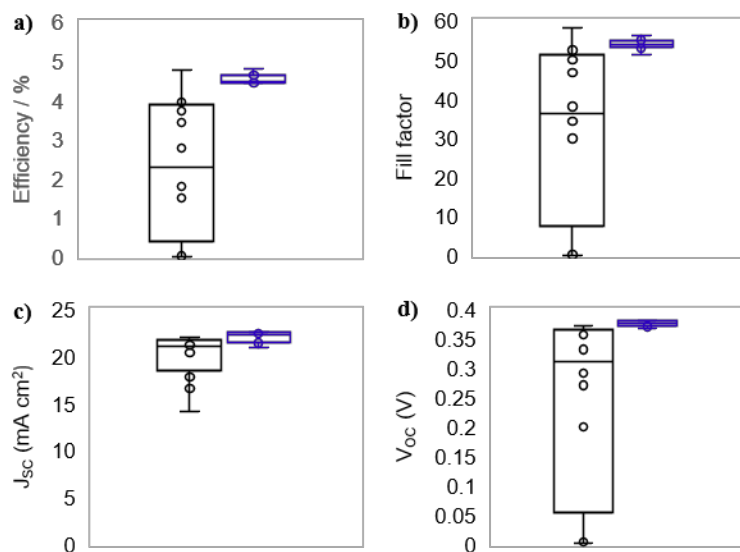


Figure 2.12 Key performance characteristics of devices using Sn(A-amd)₂ and Sn(F-amd)₂. Black: device fabricated using Sn(A-amd)₂; Blue: device fabricated using Sn(F-amd)₂.

2.4 Conclusions

Using a new room temperature liquid ALD Sn amidinate precursor capable of high quality SnS deposition at reduced temperature leads to an improvement in SnS film conformality and solar cell device yield. The ALD window for SnS using Sn(F-amd)₂ and H₂S was obtained between 65 °C and 200 °C and the reaction was found to be surface-saturated and self-limiting. Pure and stoichiometric SnS films were deposited between 65 °C and 180 °C with detectable amount of carbon at 200 °C. A decreasing growth rate with increasing temperature was observed and subsequently investigated using QCM, which showed more mass gain upon Sn(F-amd)₂ exposure and less mass loss upon H₂S exposure as temperature increases. We attribute these trends to a change in surface reaction mechanism with temperature. Additional experiments such as in-situ FTIR and mass spectrometry could be used to examine the surface chemical bonds and reacted products to further study the mechanisms.

3 Chapter 3 Crystal structures and orientations of SnS

Abstract

This Chapter studies the crystallographic phases and orientations of SnS thin films. Films with thicknesses of 30 nm to 750 nm were made by ALD at temperatures between 80 °C and 180 °C and on different substrates including amorphous silicon dioxide (a-SiO₂) and single-crystal sodium chloride (NaCl). We show that the crystal structures and orientations of the ALD-SnS thin films vary with deposition temperature, film thickness, and substrate. We confirm the presence of π -SnS in co-existence with the thermodynamically stable α -SnS and find that it is more favorable at lower deposition temperatures. The films grown on a-SiO₂ are textured and the degree of texturing increases with lower temperature or higher thickness, and the preferred phase-orientation is also thickness dependent. The films grown on NaCl (100) exhibit much higher degree of texturing and the preferred orientation is π -(400) and α -(111) & (040), contrary to the π -(111) and α -(002) that dominate films on a-SiO₂ under the same deposition conditions. The π -SnS converts to α -SnS after annealing, consistent with the metastability of the π phase. In addition, we demonstrate a proof-of-concept device made from the highly oriented SnS grown on NaCl.

3.1 Introduction

Tin monosulfide (SnS) has demonstrated strong potential as a solar cell absorber due to its large light absorption coefficient and simple binary system with only earth-abundant elements.[26, 27, 29-32, 52] These features make it promising when compared to the

commercially available CdTe and CIGS thin film solar cells and the emerging perovskite and CZTS ones. Up to now, SnS solar cells have reached efficiency up to 4.4 % (certified) using SnS deposited by ALD as the p-type absorber and nitrogen doped Zn(O,S) as the n-type buffer layer.[29] Thermally-evaporated SnS solar cells have reached efficiency of 3.9% using the same stack structure [30] and recent progress in obtaining pure and large grain SnS has shown further potential for a higher efficiency cell due to improved carrier lifetime, itself due to reduced impurity and grain boundary defects.[87]

SnS is a p-type IV-VI semiconductor, which has a thermodynamically stable orthorhombic crystal structure consisting of double layers where tin and sulfur atoms are covalently bonded in-plane and loosely connected with van der Waals forces in the out-of-plane direction. This gives rise to strongly anisotropic properties, where the electrical conductivity and Hall mobility in-plane are five to six times higher than those along the b-axis.[1] For consistency, we use the naming convention where the b axis is perpendicular to the double layer planes and the a axis is the larger in-plane lattice parameter. The orientation that has the double layers aligned perpendicular to the substrate, such as in the (101) or (001) direction, would be preferred in a solar cell, because it favors carrier transport through the absorber to be collected by the electron and hole transport layers. It has been reported that film orientation can be strongly dependent on substrate and thickness,[102] where some degree of orientation control can be managed. Yet such observation has not been sufficiently addressed in literature.

Although it may be possible to align the SnS layers in a useful fashion, an alternative approach, which eliminated the problems posed by anisotropy, would also be attractive. Also, the orthorhombic crystal structure leads to an indirect bandgap of 1.1 eV, which is 0.3 – 0.4 eV below its effective absorption onset, which could lead to noticeable loss in the open circuit

voltage. The cubic phase of SnS has long been known to the scientific community, which is isotropic and has a direct bandgap. Earlier researchers disagree about whether it is of rock-salt or zinc-blende structure.[3, 31, 33-35, 38, 65, 71, 75] A new cubic phase of SnS was reported in 2015, comprising 64 atoms in a unit cell and has a lattice constant of 11.7 Å. [19] It likely resolves the previous rock-salt/zinc-blende confusion and has since gained increasing acceptance.[4, 16, 20, 22-25, 55] In addition, solar cells made with this cubic SnS thin film by chemical bath deposition have reached an efficiency of 1.28%. [18]

It has been demonstrated that polymorphism could be induced by stress or epitaxial growth on a lattice matched substrate. Yet, such effect has not been studied much in the context of SnS. Single crystalline MgO, GaAs, Si, and NaCl have been used as lattice-matched substrates for SnS to induce epitaxy.[34, 35, 48, 57, 61] Yet, most reported epitaxial growth of the orthorhombic phase used vacuum deposition methods at relatively high temperatures during growth (150 – 400°C). The cubic phase growth was however mostly reported using solution-processing methods,[16, 20, 22, 65, 71, 73, 75] where the most commonly used epitaxy-inducing substrate, NaCl, is not suitable. In addition, although one of the ultimate intentions for making epitaxial film is to make high quality absorber for solar cell, no such demonstration has been reported. In this chapter, we examine the effect of substrate and other deposition conditions on SnS thin film crystal structure and make a solar cell out of our semi-epitaxially grown cubic SnS thin films.

3.2 Experimental

SnS was deposited by ALD using the same basic setup and precursors as described in the previous chapter. SnS films 90 nm to 750 nm thick were deposited at temperatures ranging from 80 °C to 200 °C using amorphous silicon thermal oxide or fused quartz (a-SiO₂), polycrystalline

molybdenum, and single crystal NaCl (100) as substrates to examine the effect of deposition temperature, film thickness, and substrate. Note that vacuum and purging times were shortened in some runs of deposition where relatively thick films were needed, so that the time of deposition could be manageable. The Mo substrates were obtained by sputtering 800 nm of Mo on the silicon thermal oxide substrates. All substrates except NaCl (100) ones were cleaned by rinsing in deionized water, acetone, and isopropanol, and then treated with ozone plasma for 5 min. The NaCl substrate was used as it was cleaved. The as-deposited films were annealed at 400 °C in 99.5% H₂S at 10 Torr for 1 hour in the same furnace to study their stability.

High resolution X-ray diffraction (HRXRD, PANalytical X'Pert Pro) ($\lambda = 1.542 \text{ \AA}$) θ -2 θ scans were performed on all of the films, and the peak positions were compared with the reference diffraction peak positions of α -SnS (PDF 00-039-0354), rs-SnS (PDF 01-077-3356), and π -SnS (simulated from the crystallographic information files reported by Rabkin et al.[19]) to determine the crystal phase and orientation. To examine the film texturing, 2D scans were performed in the range of $2\theta = 15^\circ - 75^\circ$ using the in-house XRD set-up ($\lambda = 1.542 \text{ \AA}$). Synchrotron-based 2DXRD ($\lambda = 0.9744 \text{ \AA}$) was performed on selected films at the Stanford Synchrotron Radiation Lightsource (SSRL), which has higher resolution and beam intensity and can thus reveal more details of the crystal structure.³⁸

Solar cells were fabricated using 600 nm of SnS deposited on NaCl (100) substrate at 120°C. Single crystal NaCl was obtained in 1 cm cubes from Ted Pella Inc. and cleaved with a razorblade into 2 – 3mm slabs to reveal a clean (100) surface. The SnS absorber layer (600 nm) and the Zn(O,S):N buffer layer were deposited at by ALD at 120°C; then 300nm of ITO was

³⁸ Hall measurements will be conducted on SnS grown at different temperatures on thermal oxide, and on the SnS grown on NaCl at 120 °C. (Indium will be used as the contact metal). Absorbance will be measured using UV-vis on a selection of samples, and Tauc plots will be obtained to derive the bandgap.

sputtered on the film to make the window layer, and 500nm of Ag was evaporated as the front contact. Details of the buffer, window, and front contact layers can be found in [29].

A transparent double-sided tape (3M Scotch 4905 VHB) was put on a quartz slide and partially coated with Ag by thermal-evaporation. Then the device stack was placed face down with its Ag pad in contact with the Ag-coated area of the tape, and the rest of the sample stuck to the clear region of the tape, as shown in the schematics in figure 3.1a-c. The NaCl substrate was then removed in de-ionized water³⁹ (figure 3.1d) and 500 nm of Ag was evaporated to the revealed SnS surface to make the back contact (figure 3.1e). However, the supporting tape was soft and the device, especially the back contact, cannot stand the pressure from the probes in the later J-V measurement, so a copper tape was subsequently used to conduct the current out of the SnS as shown in figure 3.1f. More photos of the device during the fabrication process can be found in Appendix E, as well as an alternative fabrication scheme, which has been less successful but worth further exploring.

³⁹ The substrate removal process was fast, the NaCl fell off as a large piece from the quartz slide instead of being dissolved slowly. Also, because of the imperfect NaCl cleaving, the sample was not perfectly flat, so part of the sample surface did not make tight contact with the tape.

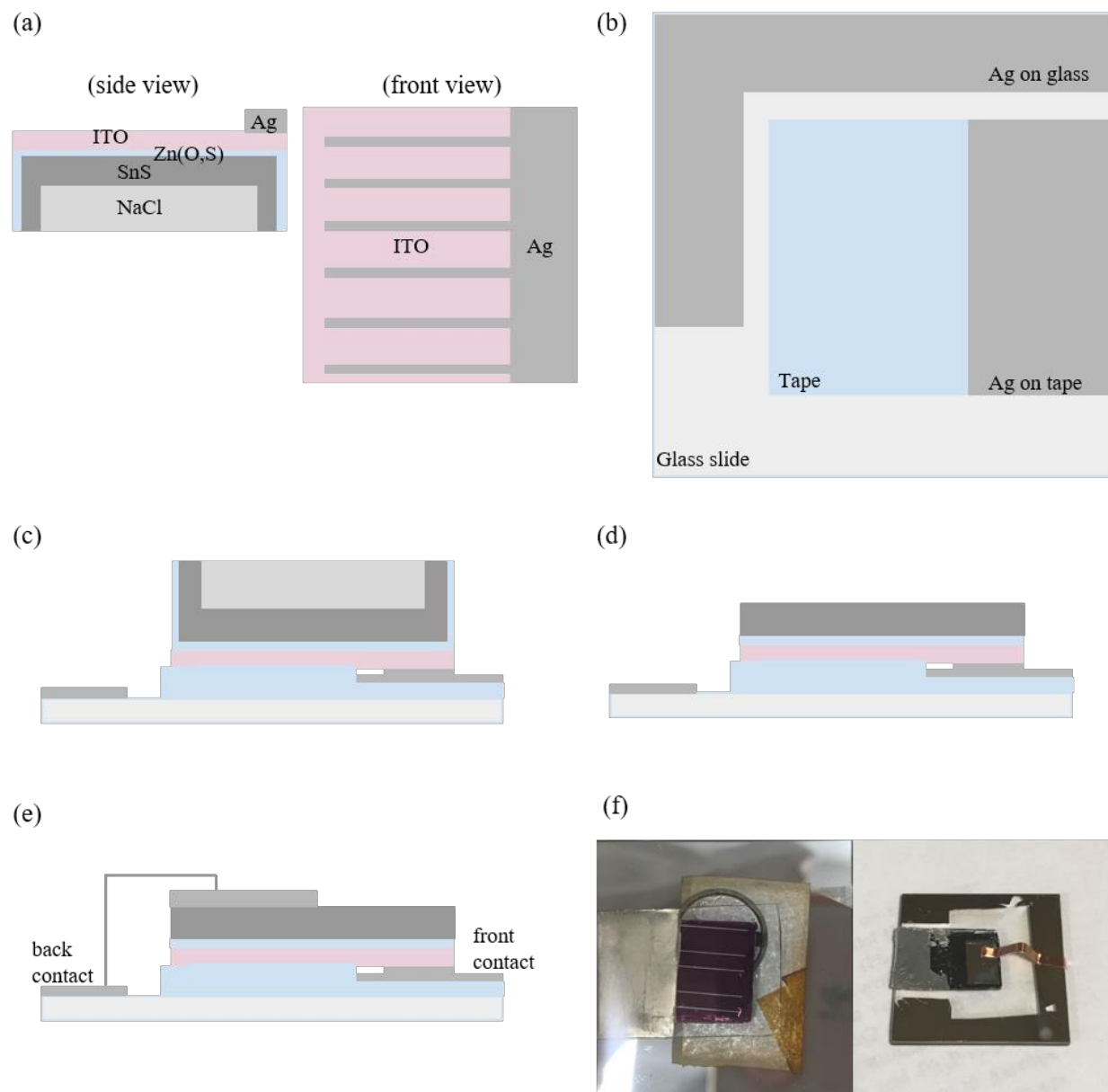


Figure 3.1 Schematics of cell fabrication procedure form SnS grown on NaCl substrate.

3.3 Results and discussion

3.3.1 Deposition temperature

Our first claim is that at lower ALD growth temperatures the as-deposited SnS adopts more of the cubic π phase, whereas at higher ALD growth temperatures the orthorhombic α phase dominates. Figure 3.2 shows the XRD θ -2 θ scans of 2000 ALD cycles of SnS thin films (90 – 150 nm) deposited on a-SiO₂ substrates at different temperatures. At a low temperature of 80 °C – 120 °C, only the π -(222) and π -(400) peaks can be seen; but as temperature increases further from 120 °C to 200 °C, the π peaks gradually disappears while the α -(120) and α -(040) peaks increase in intensity; at temperatures greater than 160°C, only the α peaks were present. This shows a phase transformation from the cubic π phase to the orthorhombic α phase as temperature increases, which has also been reported by others. [22, 23, 55, 75] The SEM images in Chapter 2 (figure 2.9 and 2.10) also show a morphology change from small crystallites resembling more of a tetrahedral shape to more plate-like grains as temperature increases.

We shall note that this out-of-plane θ -2 θ scan alone cannot fully determine the phases of a thin film, because it can only detect the planes lying parallel to the substrate. Therefore, it is possible that the $\alpha(\pi)$ -SnS phase still exist even the θ -2 θ scan does not show any $\alpha(\pi)$ -peaks, because the films are textured. Yet, this θ -2 θ scan provides direct assessment of the film orientation parallel to the substrate. We see that as temperature increased from 80°C to 120°C, the π -(222) peak decreases while the π -(400) peak becomes more apparent, eventually reaching similar intensities, indicating reduced film texturing in the π -SnS as temperature increases.⁴⁰

⁴⁰ Also note that the degree of crystallinity should not be concluded from the peak height in this set of data because the film thickness is different due to different growth rate at different temperatures as shown in the previous chapter.

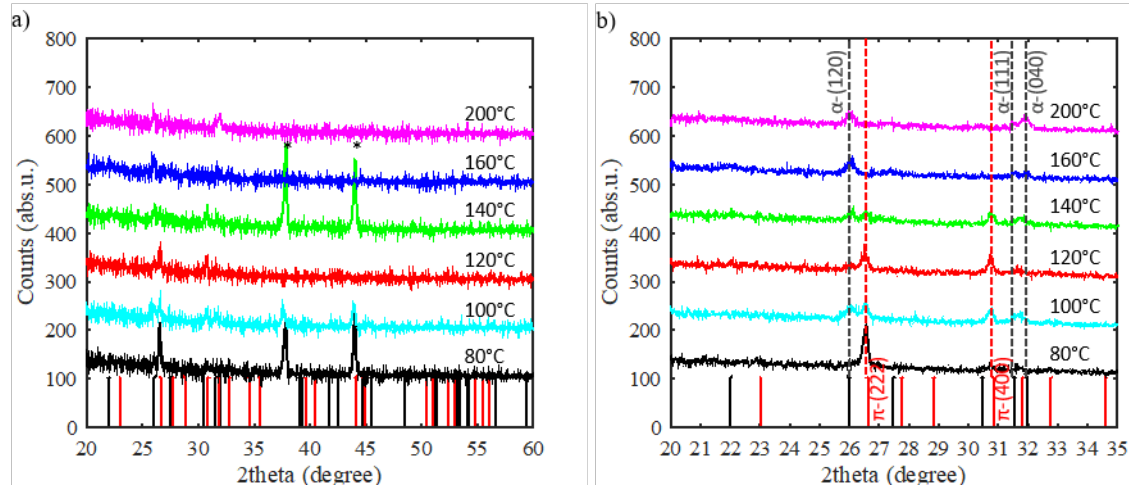


Figure 3.2 XRD θ - 2θ scans of 2000 ALD cycles (70 nm – 150 nm) of SnS deposited at 80 °C – 200 °C on thermal oxide substrate. (b) is a zoomed-in image of (a) in the range of $2\theta = 20^\circ - 35^\circ$. The asterisks (*) mark the peaks from the substrate holder of the XRD equipment.⁴¹

Thus, our second general claim is that the degree of film texturing decreases with increase in temperature. To further characterize the phases and examine the film orientation/texturing relating to temperature, 120 nm of SnS thin films were deposited at 80 °C and 120 °C and examined with the Synchrotron 2DXRD at SLAC. From figure 3.3 we see that the film deposited at 120 °C is more polycrystalline/randomly oriented, since the intensity is more evenly spread in the rings. From the XRD spectra obtained by integrating the 2D images (figure 3.4), we see that the film deposited at 80 °C shows a cleaner spectrum corresponding to the simulated π phase in terms of both peak positions and relative intensities, whereas the film deposited at 120 °C shows a less prominent π -(222) peak at 26.5° but shoulders corresponding to the α -(120) and α -(021) peaks. Also, the peak intensity around 31.8° is stronger than would be expected from simulation of the π -spectra,[20] indicating existence of the α -(111) or α -(040)

⁴¹ The substrate holder peaks were blocked by a large piece of silicon wafer for most samples, but a few samples were left out.

peak⁴² together with the π -(410) peak at 31.82° . These 2DXRD results confirm both the phase transition from π to α and the reduced film texturing as temperature increases.

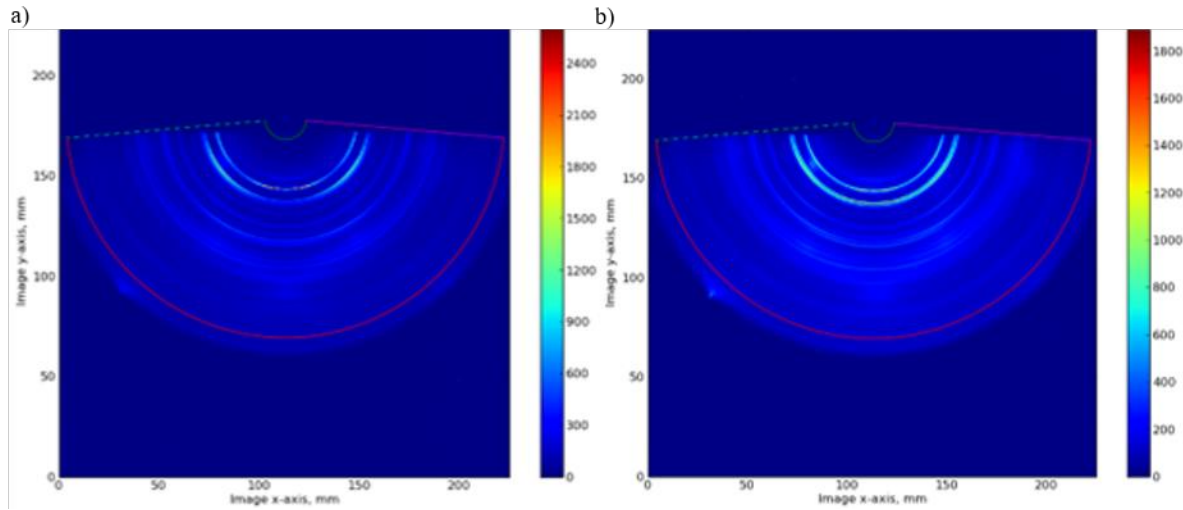


Figure 3.3 Synchrotron 2DXRD images of 120nm of SnS thin films deposited on thermal oxide substrates at (a) 80 °C and (b) 120 °C.

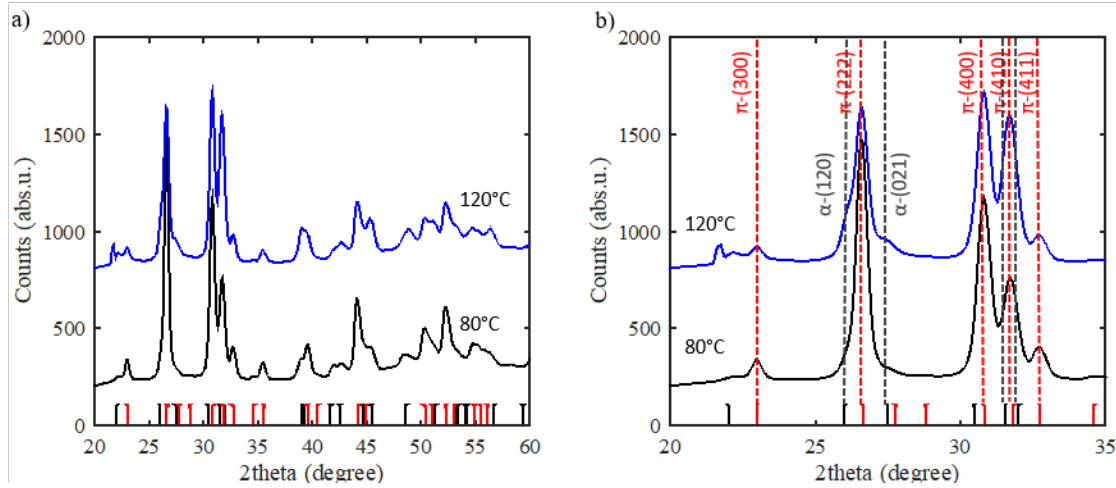


Figure 3.4. Integrated spectra from the Synchrotron 2DXRD images from $2\theta = 20^\circ - 60^\circ$. (b) is a zoomed-in image of (a) in the range of $2\theta = 20^\circ - 35^\circ$.

⁴² The α -(111) or α -(040) peaks are located at 31.53° and 31.97° respectively.

The XRD θ - 2θ scans of thicker films deposited at 80 °C – 200 °C, as presented in figure 3.6, further support the claim of reduced film texturing with increasing temperature, as more peaks with more evenly spread intensities show up in the spectra of films deposited at higher temperatures. The preferred orientation also changes from α -(002) to α -(120) and α -(021) as temperature increases from 80°C to 200°C. However, the spectra do not show the same phase transition from π to α as seen in the thinner films in figure 3.2, and the dominating peaks in the thinner and thicker films are also different at the same temperature. This thickness effect will be discussed in the next section.

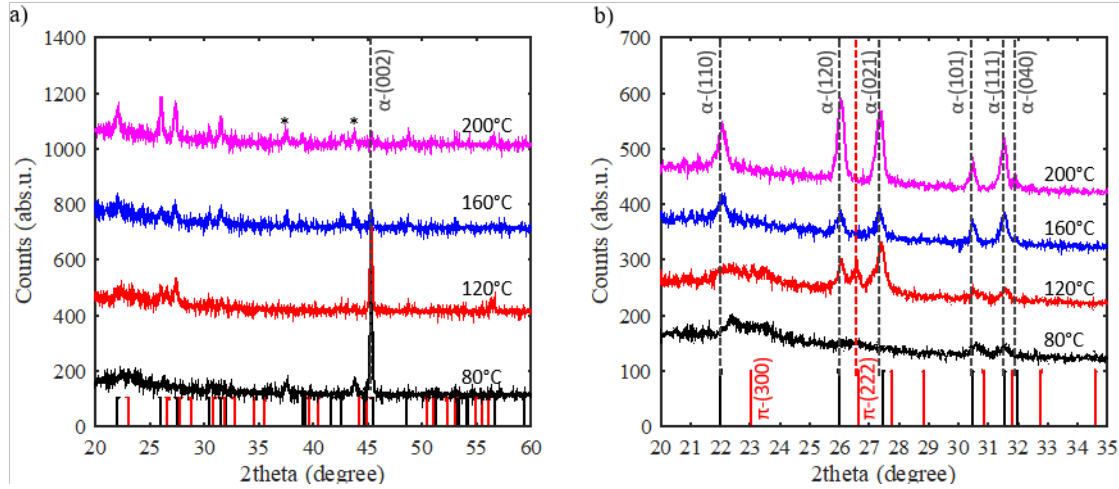


Figure 3.5 XRD θ - 2θ scans of thick SnS films (300 nm – 720 nm) deposited at 80 °C – 200 °C on thermal oxide substrate. (b) is a zoomed-in image of (a) in the range of $2\theta = 20^\circ - 35^\circ$. The asterisks (*) mark the peaks from the substrate holder of the XRD equipment.

3.3.2 Film thickness

Film thickness is found to be another factor that may cause phase transition and orientation change in SnS thin films. Comparing figure 3.2 and figure 3.5 in the previous section, we see that while π -SnS is the only phase detected by XRD θ - 2θ scans in the thinner films deposited at 80°C and 120 °C, as film thickness increases, the phase present becomes α -SnS with

α -(002) as the dominating orientation, which indicates a $\pi \rightarrow \alpha$ phase transition. At a higher temperature, although the phase present is α -SnS at all thicknesses, the preferred orientation changes with increasing proportions of the α -(110), α -(120), α -(021), α -(101), and α -(111) peaks in the thicker films, compared to the α -(120) and α -(040) oriented peak in thinner films.

Figure 3.6 shows the XRD θ - 2θ scans of SnS films of three different thicknesses deposited at 80 °C. Unlike what is reported in Sinsermsuksakul et al.,[52] where the preferred orientation changes from α -(040) to α -(111) as film thickness increases,⁴³ in our films deposited at 80°C, only the π -(222) peak is evident in the 140 nm thick film and the α -(002) peak gradually increases as thickness increases. The co-existence of both π and α phases is evident in the 320 nm thick film, but as the film thickness further increases, the π -peak intensity keeps decreasing and the α -(002) becomes the only dominating peak. This result is consistent with a transformation from π -SnS to α -SnS as film thickness increases. However, it could also be caused by film orientation changes: while both phases exist, the α -{002} planes become parallel to the substrate while the π -{222} planes become mis-orientated as film thickness increases. The absence of other peaks indicates high degree of film texturing, resulting in less straightforward phase identification. More advanced techniques such as GIXRD or 2DXRD need to be done on this set of films to further examine the phase and orientation change with thickness.

⁴³ In their α -SnS films deposited using Sn(A-amd)₂ and H₂S at 200 °C

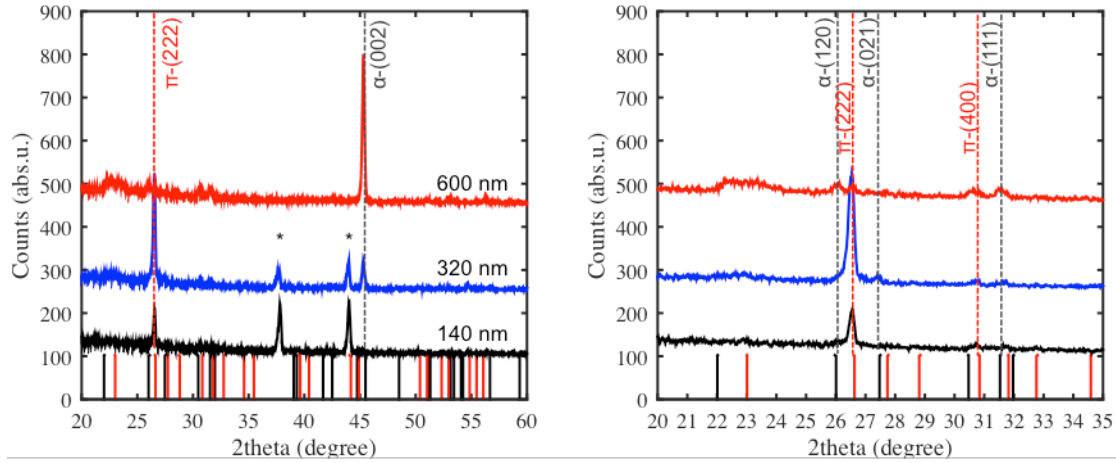


Figure 3.6 XRD θ - 2θ scans of 140 – 600 nm of SnS deposited at 80°C on thermal oxide substrate. (b) is a zoomed-in image of (a) in the range of $2\theta = 20^\circ - 35^\circ$. The asterisks (*) mark the peaks from the substrate holder of the XRD equipment.

We speculate that this orientation change might be related to the surface energies of the different facets of π -SnS or α -SnS. According to Stevanovic et al., [85] the surface energies rank in the order of $\gamma_{(040)} < \gamma_{(120)} < \gamma_{(111)} < \gamma_{(131)} < \gamma_{(021)} < \gamma_{(002)}$ for the facets corresponding to peaks that appears most often in the α -SnS XRD patterns,⁴⁴ and presumably in the order of $\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)}$ for π -SnS given that it is a derivative of the rock-salt structure. Based on the argument by Sinsermsuksakul et al.,[52] we propose the following explanation: when the films is thin, the lowest energy facets would be exposed to the surface and the film should thus be oriented in the (111) direction for the π phase and (040) direction for the α phase; as film thickness increases, grain boundaries gradually dominate the surfaces and interfaces, and the π -(111) and α -(040) facets thus should be oriented more parallel to the grain boundaries, which could lie relatively perpendicular to the substrate due to initial nucleation and island growth.

⁴⁴ This order of surface energy is in general agrees with that for a face-centered cubic structure, which the orthorhombic α -SnS is a distorted version of.

This surface energy based argument can explain to some extent explain the transition away from the π -(111) and α -(040) orientations as film thickness increases but is insufficient for the complex phase and orientation changes observed in this work. For α -SnS, the differences between all facets other than (040) are relatively small, and the (040) surface energy is much lower than the others due to the van der Waals bonded double layers; and there is no report available on the surface energies of π -SnS. At this moment, we do not have an adequate hypothesis to fully explain our results. It would be interesting to further explore the phase transition and orientation change in connection to the growth mechanisms discussed in Chapter 2 in the future.

3.3.3 Annealing

Nonetheless, we have obtained highly-oriented 600 nm thick α -SnS films at 80 °C and 120 °C with the double layers aligned perpendicularly to the substrates as shown in figure 3.5, which is desired for a solar cell. Since in our standard solar cell fabrication procedure an annealing step is essential, the films deposited at 80 °C and 120 °C (from the same batch as the films in figure 3.6) were annealed at 400 °C in an H₂S environment and examined with XRD. It is shown in figure 3.7 that the desirable α -(002) orientation remains unchanged at lower temperature while significant grain growth with orientation (120) and (021) was observed at higher temperatures. The misalignment from the (002) orientation means that the α -SnS double layer changes from vertically aligned to the substrate to half-parallel, which is less desirable for solar cells. Therefore, a lower deposition temperature is desired for the sake of obtaining a film orientation suitable for carrier transport through the absorber.

However, film deposited at 80°C flaked off during annealing, while film deposited at all higher temperatures remained conformal. This is possibly due to the high amount of unreacted –

SH groups in the films at low deposition temperature, which recombined to form H₂S gas upon annealing, and the de-gassing process cause the round bubble-like features in figure 3.8. Longer vacuum and purging times (20s/40s) and lower temperature annealing have been tried. Less flaking was observed but not completely removed, and the resulting smaller grain size caused higher series resistance and lower efficiency in the device.

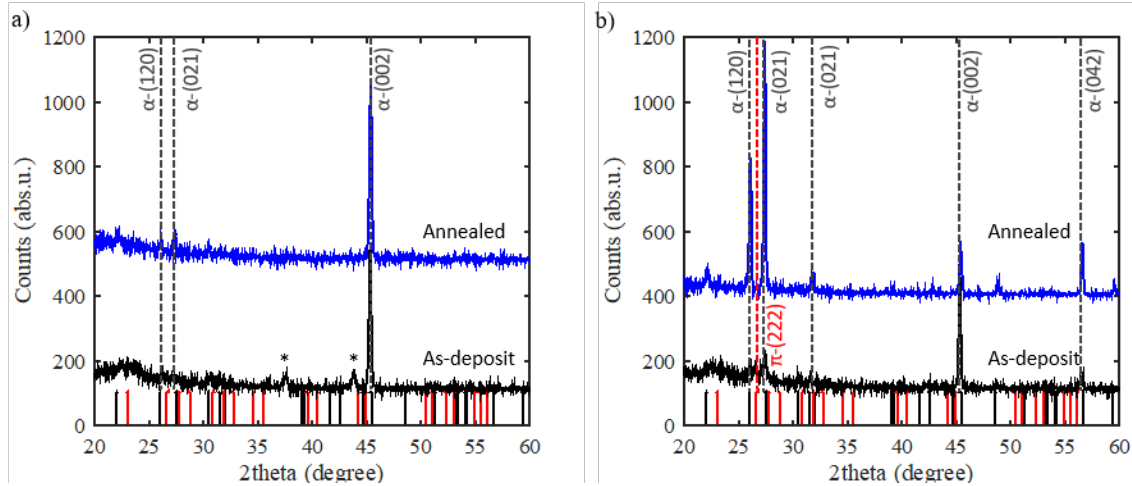


Figure 3.7 XRD θ - 2θ scans of as-deposit and annealed thick (>600 nm) SnS films (a) deposited at 80 °C and (b) deposited at 120 °C on thermal oxide substrate. The asterisks (*) mark the peaks from the substrate holder of the XRD equipment.

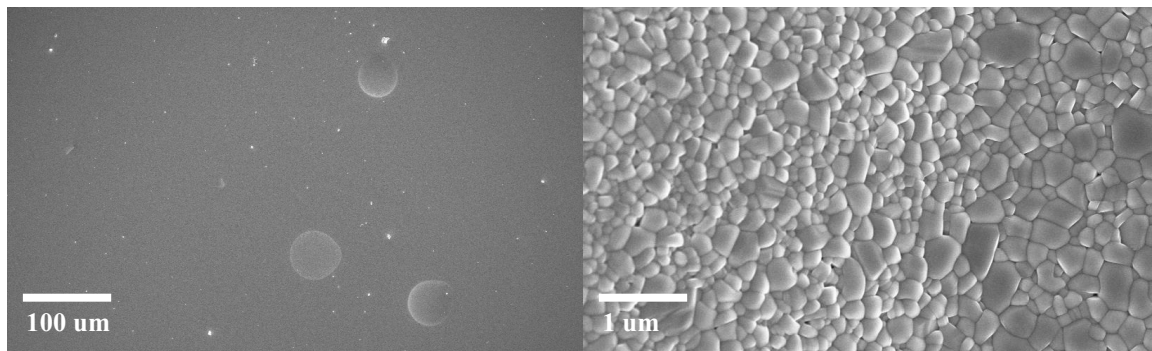


Figure 3.8 SEM image of annealed film (400°C, 1hr, H₂S) deposited at 80°C on thermal oxide substrate. As indicated by the scale bar, (b) is a zoomed image of (a).

3.3.4 Pressure of H₂S and other deposition parameters

We have also observed that the SnS phase and orientation are dependent on the H₂S exposure during the deposition. Figure 3.9 shows the XRD θ -2 θ scan of two thick films (> 600 nm) of SnS deposited at 120°C with one and two doses of H₂S, which was equivalent to 0.5 torr·s vs. 1.5 torr·s of H₂S exposure. We see that the π -(222) peak intensity increase significantly with H₂S, indicating either an increased share of π phase in the film, or a change in the π -phase orientation so that the previously misaligned π -(222) planes are now aligned parallel to the substrate.

Bilousov et al. [23] reported that the amount of α -SnS increase with decrease in H₂S exposure in their mixed phase film deposited by ALD at 120°C. They also found that the amount of π -phase remains at least 40% even with the shortest H₂S exposure time. Therefore, it is unlikely that in my case the π -phase could be almost eliminated by reducing from two doses of H₂S to one, so it is more likely that both films are textured and the increase in H₂S exposure changes the orientation of the π phase crystallites. Also, the two films were not initially designed to be compared, so the film thickness and vacuum/purging times were slightly different. It is possible that the thickness also contributed to the orientation change as discussed in the previous paragraphs. To further examine the effect of precursor and recipe, more careful set of experiment should be designed, and GIXRD or 2DXRD shall also be used to fully examine the phases and orientation.

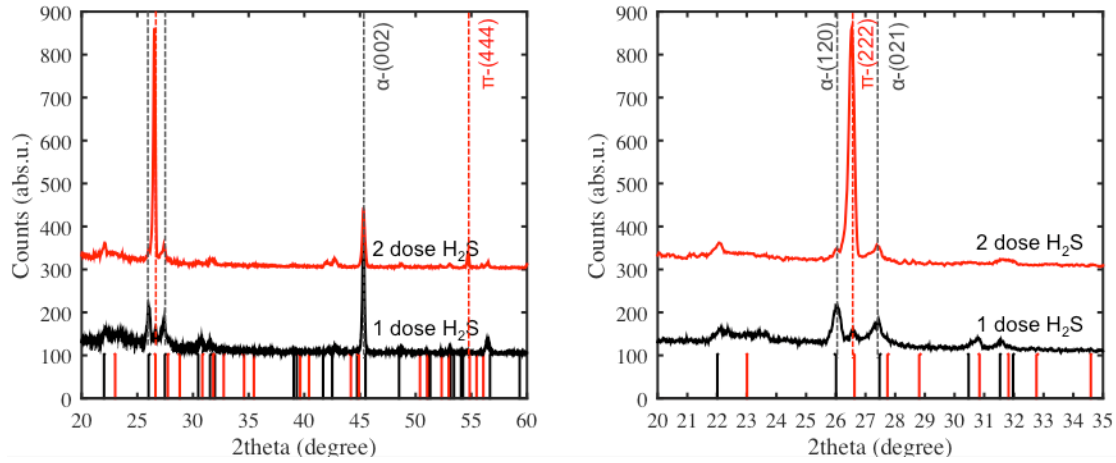


Figure 3.9 XRD θ - 2θ scans of thick (>600nm) of SnS films deposited at 120°C using different number of H₂S doses, (b) is a zoomed-in image of (a) in the range of $2\theta = 20^\circ - 35^\circ$.

3.3.5 Epitaxial growth on lattice-matched substrate

From the results above, we see that it is difficult to obtain a π -phase film suitable for solar cell applications. π -SnS tends to form at lower temperatures as shown in figure 3.2 – 3.4 and is likely to be preferred in thinner films as shown in figure 3.6; it is also not stable under the annealing conditions previously used for grain growth in solar cell fabrication as shown in figure 3.7. However, low temperature leads to smaller grains and a working solar cell needs at least a few hundred nanometers to absorb light and be robust enough to avoid shunting. Therefore, an alternative need to be found to achieve high quality π -SnS for solar cell applications. Here we explore a lattice-matched substrate to induce epitaxial growth of π -SnS.

NaCl (100) is the most used substrate in the limited literature found on epitaxial growth of SnS. Although NaCl has a lattice constant of 5.64 Å (PDF 05-0628), causing a mismatch of less than 3% with the previously reported rock-salt SnS (PDF 01-077-3356, $a = 5.80\text{Å}$) and less than 4 % with the new π -SnS ([19], $a = 11.7\text{Å}$), it was only reported to have induced epitaxial growth of α -SnS.[34, 35, 48] Other epitaxy inducing substrates tested for SnS are MgO (100) and graphene,

but again they are reported for the growth of α -SnS.[57, 61] The orientation reported is α -(040) in all epitaxial SnS cases. Encouraged by the cubic SnS grown on the amorphous thermal oxide substrate as in figure 3.2 and 3.9, I grew a thick film of SnS on the NaCl (100) surface, with the hypothesis that the lattice matched NaCl substrate would induce epitaxial growth of π -SnS.

Figure 3.9 shows the XRD θ - 2θ scans of 12000 cycles of SnS deposited on NaCl (100) and thermal oxide substrates. We see that while the peaks corresponding to π -(222) in both samples are nearly the same, π -(400) become the dominant peak in the sample deposited on NaCl, which has an intensity more than an order of magnitude larger than the π -(222) peak, indicating high degree of epitaxial film growth of the π -SnS in the $\langle 100 \rangle$ direction. SEM images comparing those two samples also show differences in morphology. The film grown on SiO_2 substrate shows columnar grains with visibly smaller grain size, especially in the region near the substrate. The film grown on NaCl shows larger grain size and better epitaxial features, and it is also slightly thinner compared to that grown on thermal oxide, possibly due to slow initial nucleation. These results agree with our hypothesis that the NaCl (100) surface induces epitaxial π -SnS growth in the corresponding orientation.

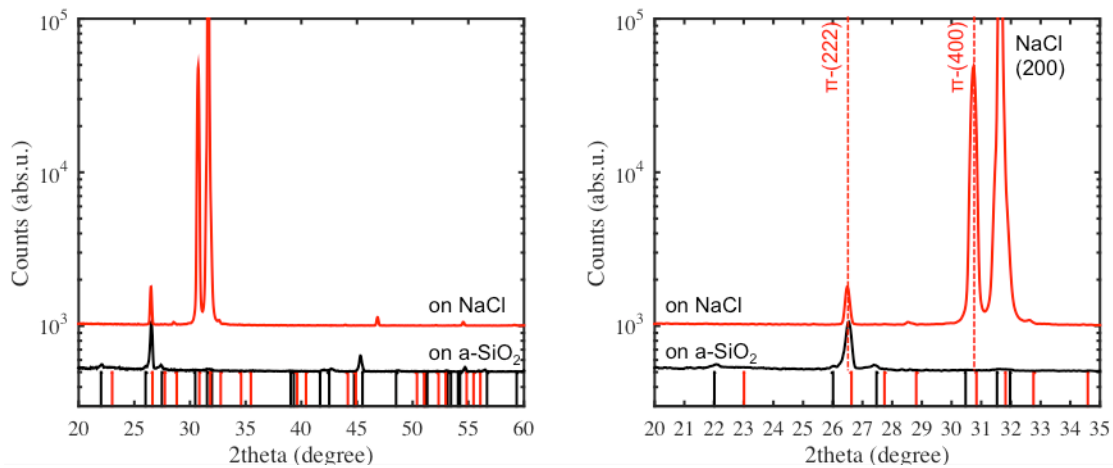


Figure 3.10 XRD θ - 2θ scans of 12000 cycles of SnS films deposited at 120°C on thermal-oxide and NaCl (100) substrates. (b) is a zoomed-in image of (a) in the range of $2\theta = 20^\circ - 35^\circ$.

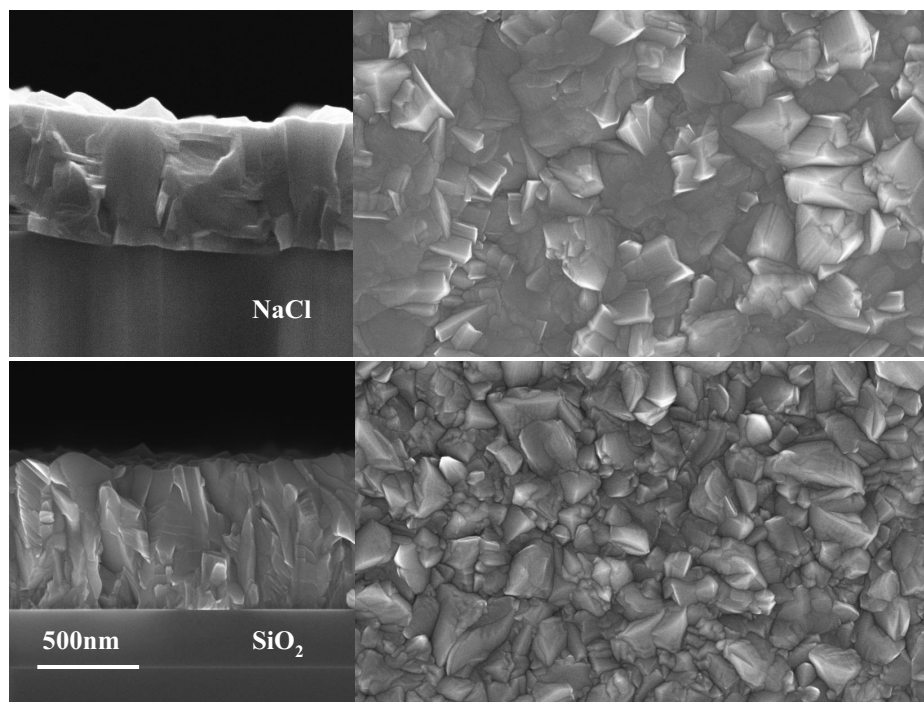


Figure 3.11 SEM of 12000 cycles of SnS deposited NaCl (100) and thermal oxide substrate.

However, the NaCl (200) substrate peak overlaps with several major SnS peaks of both the α and π phase, and those peaks might have been obscured by the substrate peak. XRD θ - 2θ scan was taken again after dissolving the substrate in water and presented in figure 3.12. Two peaks in the region of $31.5^\circ - 32^\circ$ appeared, which aligns well with the α -(111) (31.53°) and α -(040) (31.97°) peaks, although we cannot rule out the existence of π -(410) peak at 31.82° .

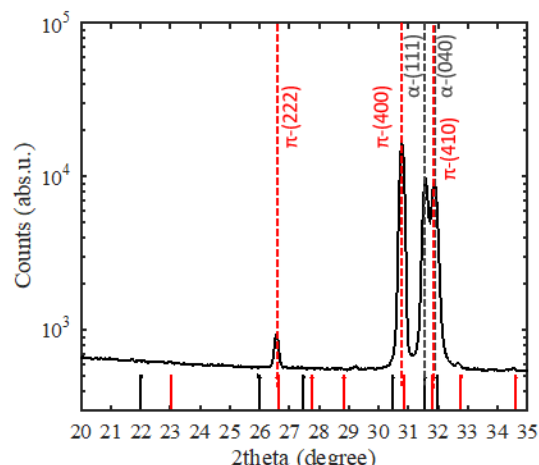


Figure 3.12 High resolution XRD of 12000 cycles of SnS films deposited at 120°C on NaCl (100) - after removing the substrate.

The synchrotron 2DXRD image (figure 3.13) shows that while the film grown on thermal oxide is highly textured, the film grown on NaCl shows almost single-crystalline features of spots, instead of rings or parts of rings. Yet, integrating the 2D spectra, we see peaks corresponding to both α and π phases (figure 3.14). Therefore, we conclude that the films are of mixed phase on both NaCl and SiO₂ substrate. NaCl induces high of degree of epitaxial growth in the $\langle 100 \rangle$ direction of the π phase, while the $\{111\}$ planes are oriented near-randomly, as manifested in the corresponding dots and rings. But on SiO₂, the dominating orientation is the $\{111\}$ planes parallel to the substrate, and the films is highly textured but not epitaxial.

After annealing in H₂S at 400°C for 1 hour, the mixed phase film converted near completely to the α phase regardless of the substrate.⁴⁵ As estimated from the reference crystallographic information (PDF 00-039-0354 for α -SnS and from [19] for π -SnS.), the unit cell size of α -SnS is 192.7 Å³ and consists of 8 atoms; the unit cell of π -SnS is 1601.6 Å³.

⁴⁵ The film on NaCl went through delamination after annealing, and the delamination worsened dramatically after sitting in the air for a few hours.

Therefore, the atomic density of α -SnS (41.62 nm^{-3}) is calculated to be 3.9% higher than that of π -SnS (39.96 nm^{-3}). Note that this change in atomic density, although small, could potentially lead to cracks forming during annealing due to the $\pi \rightarrow \alpha$ transition.

As shown in figure 3.12 and 3.13, the previous dominating π -(222), (400), and (510) peaks disappear almost completely on both SiO_2 and NaCl , and we see significant growth of α -(120), (021), (101), and (111) peaks. The film on NaCl still shows more single-crystallinity features compared to the annealed film on SiO_2 , as seen in the 2D images, despite the rings feature of a polycrystalline film become more prominent after annealing. This film should be described as textured α -SnS film with (101) and (111) as preferred orientation. The film on SiO_2 is also textured after annealing, but in a different way. As shown in Figure 3.12 (d), the preferred orientations are (110), (120), (021), and (002), while the (101) and (111) peaks are not detected parallel to the substrate. This result agrees with the XRD θ -2 θ scan of the annealed film in Figure 3.6(b), although the samples are deposited in different batches where the H_2S doses was different.

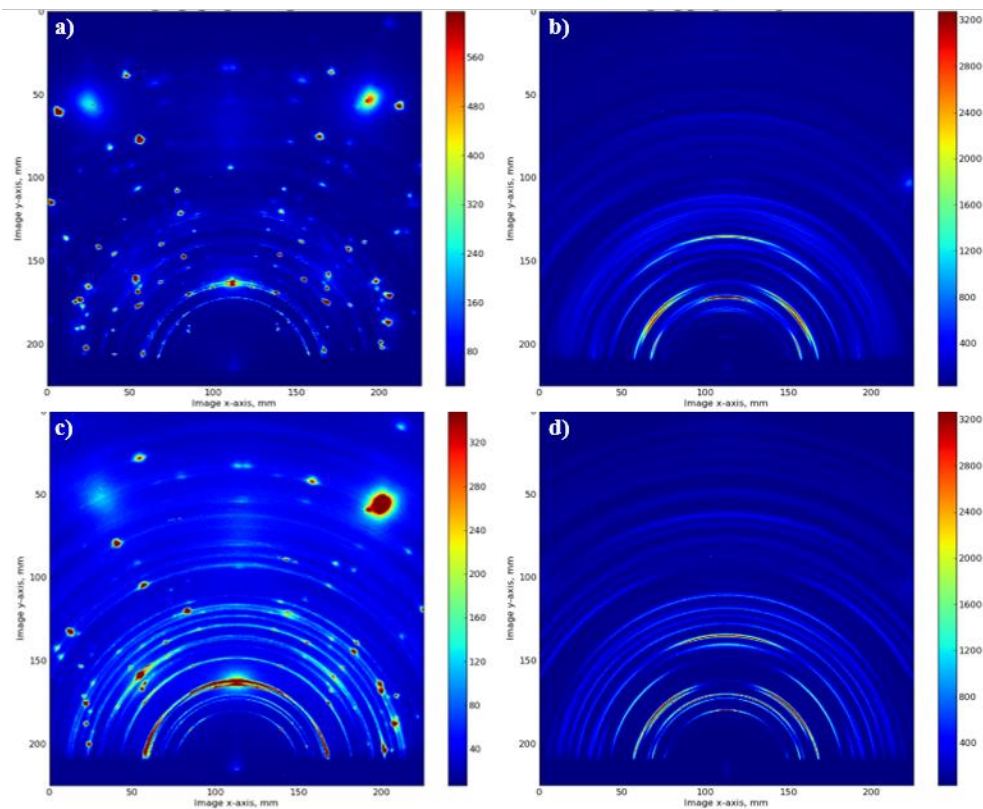


Figure 3.13 SLAC-2DXRD of 12000 cycles of SnS films deposited at 120°C. (a) as-deposit on NaCl (100) substrate (b) as-deposited on thermal-oxide substrate (c) annealed on NaCl (100) substrate (d) annealed on thermal oxide substrate.

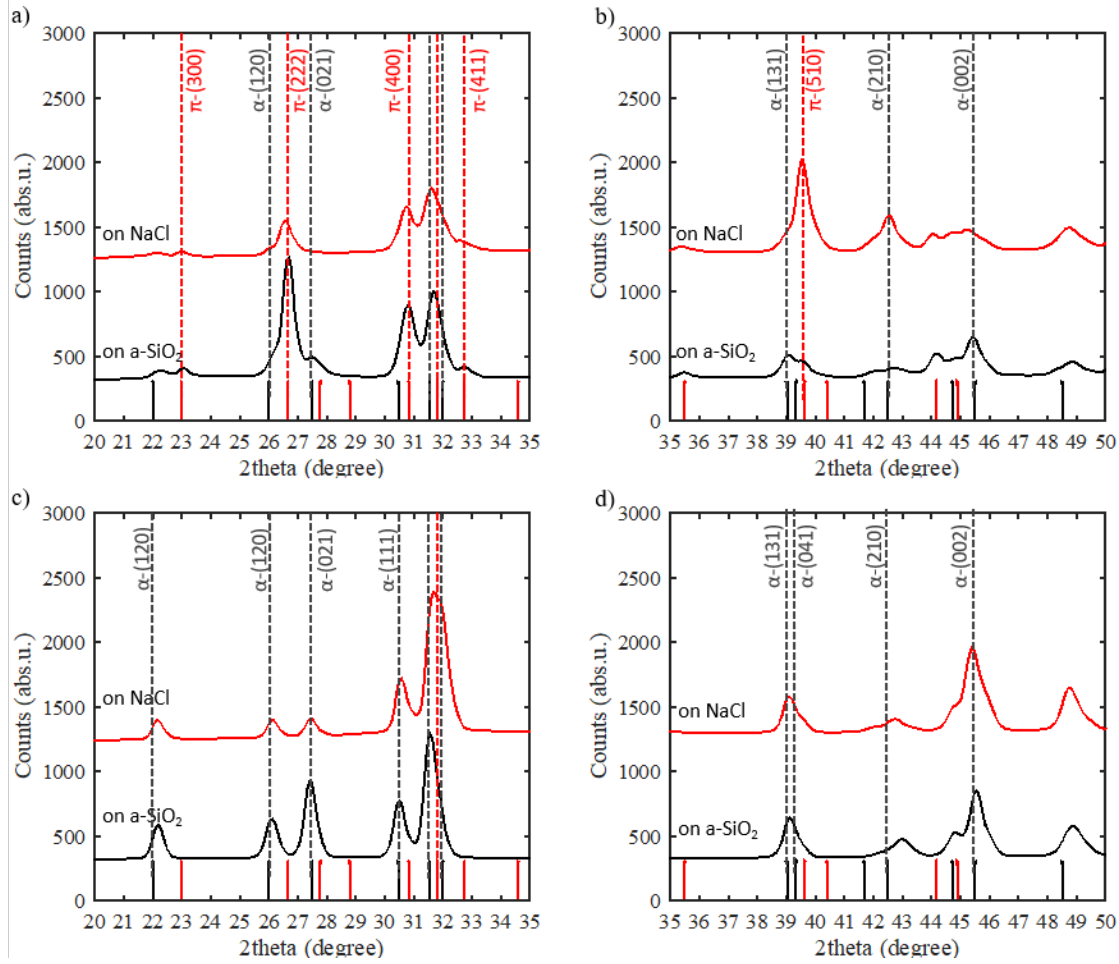


Figure 3.14 Integrated spectrum from SLAC-2DXRD of 12000 cycles of SnS films deposited at 120°C on thermal-oxide and NaCl (100) substrates. (a) as-deposit, (b) a zoomed-in image of (a) in the range of $2\theta = 20^\circ - 35^\circ$, (c) annealed, (d) a zoomed-in image of (c) in the range of $2\theta = 20^\circ - 35^\circ$.

3.3.6 Device performance

A solar cell was fabricated using the epitaxially grown SnS on NaCl and its I-V results are presented in figure 3.15. The device shows diode behavior, although fairly bad ones. The nominal open circuit voltage demonstrates large variance from 96 mV to 670 mV with the

majority results in the range of 200 – 250 mV in the 10+ measurements.⁴⁶ The short circuit current is on the order of 100 nA/cm², which is 5 orders of magnitude lower than that of a normal functioning solar cell of about 20 mA/cm² made from α -SnS. This poor performance cannot be solely accounted for by the increase bulk resistance of the π -SnS. The high series resistance could be due to the low quality of front and back contact, which also causes the large variation between measurements. We should also note that the seemingly high V_{OC} could be due to a capacitance effect, and a $SunV_{OC}$ measurement could be conducted to further examine this effect. Nonetheless, this cell was determined not to be further studied due to the unreliable contacts. The solar cell characterization techniques would be more informative after we improve the contact quality and obtain the optical and electrical properties of the π - or mixed phase SnS.

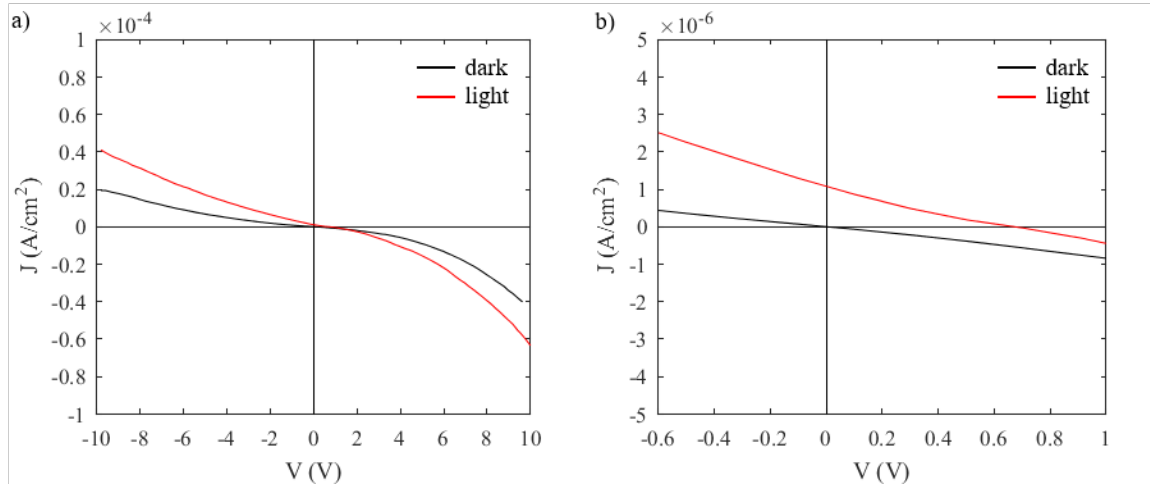


Figure 3.15 Dark and light IV measurement of the device above. (b) is a zoomed in image of (a).

⁴⁶ It is seen that the result depends highly on the location where the probe is in contact with the front and back contact and pressure applied.

3.4 Conclusion

In summary, it is demonstrated that the phase and orientation of an SnS film are determined by the combined effect of temperature, film thickness, precursor, and substrate. The film grown on a-SiO₂ is textured but the degree of texturing decreases as temperature increases, and the preferred phase-orientation is dependent on both thickness and temperature. Whereas the π -(222) peak dominates thinner films, the α -(002) peak dominates thicker ones at low temperatures. Highly oriented SnS films can be obtained by growing on a lattice matched NaCl (100) substrate, even though the film is of mixed α and π phases. For future studies, one can further optimize the deposition conditions to obtain phase-pure epitaxial or preferably orientated SnS films to achieve better carrier transport properties through the solar cell absorber. Devices fabricated from the SnS grown on NaCl show potential improvement of the open circuit voltage. Yet challenges remain in reducing the series resistance of the cell and improving the contact quality as well as the reliability of the fabrication process.

4 Chapter 4 Other related works and future directions

Abstracts

This Chapter delineates several additional approaches to understanding and improving SnS solar cells by addressing different layers of the device. First, it is important that the metal used for back contact forms a low resistance ohmic contact with the p-type SnS. Thus, we systematically investigated the interfaces between SnS and three metals (Au, Mo, and Ti) commonly used for contact with semiconductors. Second, we experimented with two disruptive routes to make the absorber: anion-exchange with SnO, and alloying with CaS. Third, we attempted aluminum and indium doping of the Zn(O,S) buffer layer to enable independent adjustment of carrier concentration and conduction band offset. Lastly, we added an anti-reflection coating layer to solve the issue of high reflective loss of the device and consequently increased the photocurrent. The last section summarizes this thesis and identifies a few directions for future work.

4.1 Study of the metal/SnS contact resistance

Content in this section (4.1) has been published in Journal of Applied Physics 122(4): 045303;

DOI: 10.1063/1.4992086

Yang, C., L. Sun, R. E. Brandt, S. B. Kim, X. Zhao, J. Feng, T. Buonassisi and R. G. Gordon (2017). "Measurement of contact resistivity at metal-tin sulfide (SnS) interfaces." [102]

We measured the contact resistivity between tin(II) sulfide (SnS) thin films and three different metals (Au, Mo, and Ti) using a transmission line method (TLM). The contact resistance increases in the order $\text{Au} < \text{Mo} < \text{Ti}$. The contact resistances for Au and Mo are low

enough so that they do not significantly decrease the efficiency of solar cells based on SnS as an absorber. On the other hand, the contact resistance of Ti to SnS is sufficiently high that it would decrease the efficiency of a SnS solar cell using Ti as a back-contact metal. We further estimate the barrier heights of the junctions between these metals and tin sulfide using temperature-dependent TLM measurements. The barrier heights of these three metals lie in a narrow range of 0.23–0.26 eV, despite their large differences in work function. This Fermi level pinning effect is consistent with the large dielectric constant of SnS, and comparable to Fermi-level pinning on Si. The contact resistivity between annealed SnS films and Mo substrates under light illumination is as low as $0.1 \text{ } \Omega \cdot \text{cm}^2$.

4.2 Alternative routes for absorber fabrication

Despite the efforts understanding its formation mechanism and controlling its crystal structures as detailed in previous chapters, there are some intrinsic properties of SnS that limit to how much we can improve the material quality. First, the sulfur vacancy (V_S) is likely to be formed during growth or annealing due to the low formation of V_S energies under near stoichiometric conditions.[13, 17, 84] Also, although the cubic SnS can be obtained, it is unstable and converts to α -SnS upon annealing, which is a common practice in obtaining high quality crystals, and the anisotropic properties of the α -SnS is an undesirable feature in solar cell as discussed in Chapter 3. In this section, we explore the possibilities of eccentric doping to passivate V_S and alloying to stabilize the cubic SnS phase.

4.2.1 Atomic layer deposition of SnO and conversion to SnS

Oxygen might be a possible source to passivate V_S . Previous lab members have tried to incorporating $\text{Sn(A-amd)}_2/\text{H}_2\text{O}$ into the $\text{Sn(A-amd)}_2/\text{H}_2\text{S}$ cycles and found no detectable O by XPS when the fraction of $\text{Sn(A-amd)}_2/\text{H}_2\text{O}$ was small ($<10\%$). When we increased the Sn(A-

amd)₂/H₂O cycle to Sn(A-amd)₂/H₂S cycle to 1:1, small amount of oxygen was observed, but the morphology changes significantly from the previous granular shape to flakes as shown in figure 4.1, rendering it unusable for solar cells.

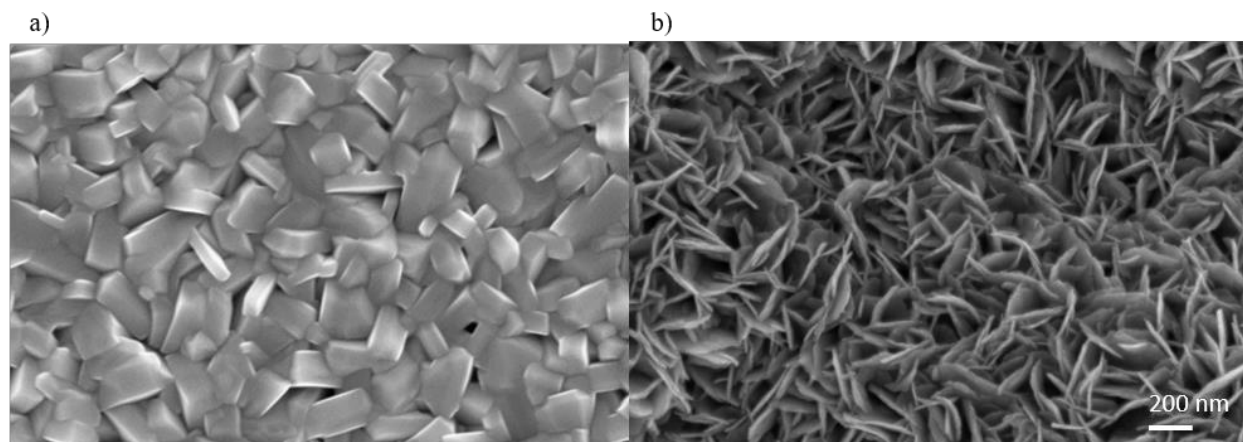


Figure 4.1 SEM images of (a) SnS film and (b) Sn(O,S) film with dosing ratio of SnO:SnS = 1:1.

Since the reaction $\text{SnO} + \text{H}_2\text{S} \rightarrow \text{SnS} + \text{H}_2\text{O}$ is exothermic and thermodynamically favorable⁴⁷, we attempted a less common approach of making SnS by annealing SnO in an H₂S environment, in the hope that a conversion would happen with small amount of O left in the film that can help passivate the V_s.

⁴⁷ Using the data from the CRC Standard Thermodynamic Properties of Chemical Substances, we calculate the free energy change of this reaction to be $\Delta G^\circ = -41.6 \text{ kJ/mol}$ under standard conditions. The entropy change can also be calculated: $\Delta S^\circ = 2.8 \text{ J/mol} \cdot \text{K}$, as well as the enthalpy change: $\Delta H^\circ = -40.5 \text{ kJ/mol}$. The free energy of this reaction at our annealing temperature (673 K) is then calculated to be $\Delta G = \Delta H^\circ - T\Delta S^\circ = -40.6 - 0.673 \cdot 2.8 = -42.5 \text{ kJ/mol}$, assuming ΔH° and ΔS° does not change appreciably with temperature. Hence, we confirm that this reaction is thermodynamically favorable, especially at elevated temperatures.

Source: CRC	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol·K)	C_p (J/mol·K)
SnO (s)	-280.7	-251.9	57.2	44.3
SnS (s)	-100.0	-98.3	77	49.3
H ₂ S (g)	-20.6	-33.4	205.8	34.2
H ₂ O (g)	-241.8	-228.6	188.8	33.6

SnO was deposited by ALD with a similar set up as SnS as described in Chapter 2, with the H₂S tank replaced an ampule that contained de-ionized water at room temperature, and at a deposition temperature of 120 °C using 1000 and 5000 cycles of Sn(F-amd)₂/H₂S. SEM was used to examine the film morphology and thickness, which was then confirmed with X-ray Reflectance (XRR). The film composition was examined by XPS and the crystal structure by XRD.⁴⁸ Then the SnO film was annealed in 4% H₂S at 400 °C for one hour under approximately 30 torr of total pressure. The resulting sample was examined with XPS and SEM for composition and morphology.

Figure 4.2 shows the XPS analysis of a 125 nm thick as-deposit SnO film. We see that the film is pure and stoichiometric SnO, with no other elements detectable by XPS initial Ar-sputtering to remove the surface contaminants. It takes longer sputtering to eventually reach the stoichiometric value of Sn:O = 50:50 due to oxidation of the surface. Valance scan (figure 4.2b) of the film after 120s of Ar-sputtering also indicates SnO as opposite to SnO₂ when compared with reference data as shown in the inset image.

⁴⁸ Ellipsometry was also conducted to measure its optical properties (n & ϵ), but the modeling process was challenging because there is no previous model for this material to base the analysis on, so the Ellipsometry data are still waiting to be analyzed. Hall measurement was also conducted but the film was too resistive, and the contact might need to be further optimized to give reliable results. I want to do an UV-vis measurement to assess the bandgap and absorption of SnO if time allows.

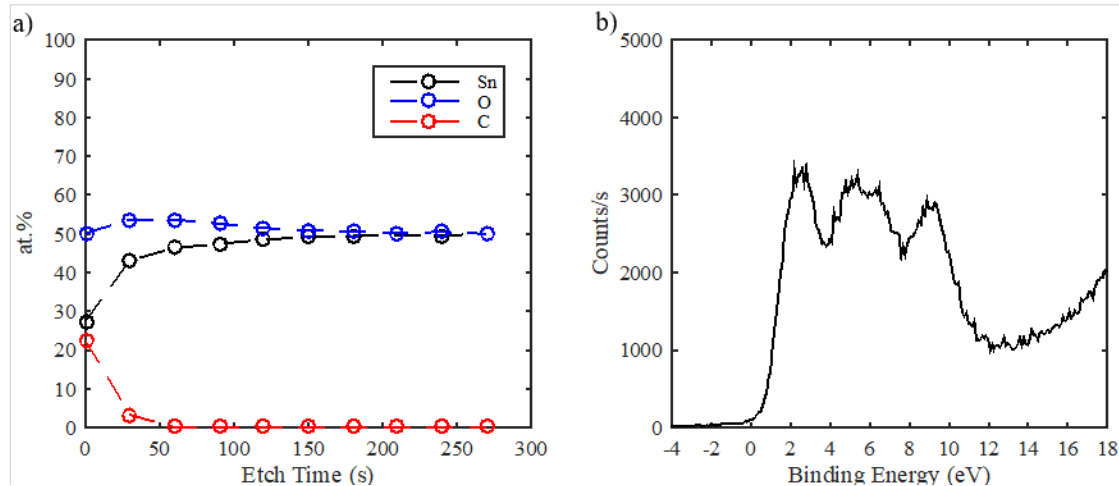


Figure 4.2 XPS results of SnO. (a) films composition vs. Ar-sputtering time, and (b) valence scan after 120s of sputtering.

Figure 4.3a shows that the as-deposit SnO film is smooth and conformal with no visible grains seen in SEM. XRD also does not show any diffraction peaks, indicating an amorphous film. However, after annealing in H_2S , the film seems to have aggregated into islands, and XPS shows that it is largely converted to SnS. We see that the amounts of Sn and S are roughly the same with Sn slightly in excess, possibly due to preferential sputtering of S. However, we cannot be certain that the conversion is complete due to exposure of SiO_2 substrate to the XPS scan, as shown by the large amount of Si and O. A thicker starting film of SnO should be used next time to better study this conversion process.

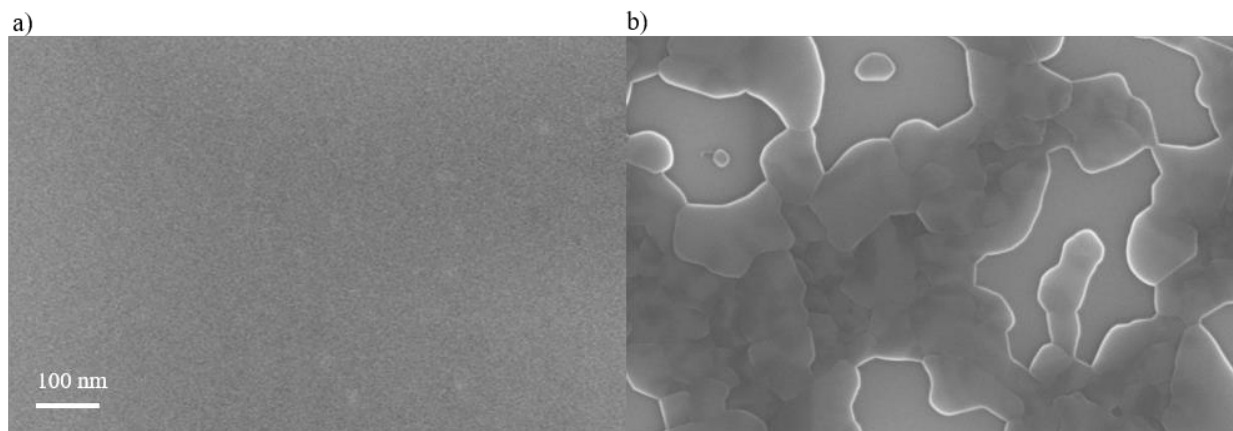


Figure 4.3 SEM image of (a) as-deposit SnO film using 1000 ALD cycles (25nm) and (b) the film in (a) after annealing in H₂S.

The growth rate of SnO was found to be 0.25 Å/cycle at 120°C, which is less than half of that of SnS, and therefore no SnS solar cell was attempted due to the long deposition time required to obtain a reasonable thickness for absorber in the scope of this project. This work only serves as a preliminary study to demonstrate the possibility of making SnS from SnO.

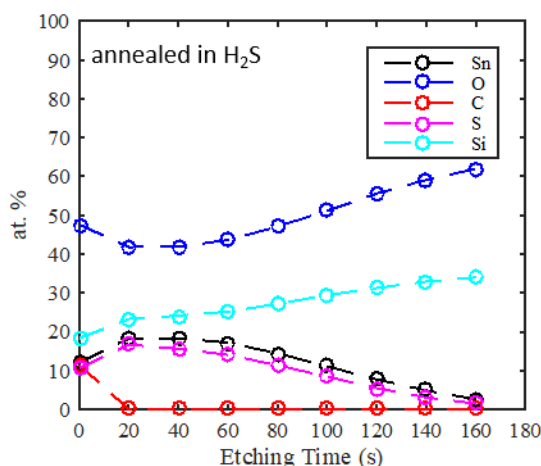


Figure 4.4 Composition of a 25 nm SnO samples annealed in H₂S.

4.2.2 Atomic layer deposition of cubic (Ca,Sn)S alloy films

This work was done in collaboration with Dr. Chuanxi Yang, and manuscript is in preparation.

We grow cubic phase (Sn,Ca)S tertiary film by atomic layer deposition and demonstrate the metastability of this chalcogenide material. Compact and smooth films are obtained only when the two metal sources share the same ligands. Compositional and quartz crystal microbalance results indicate that CaS cycle has an etching effect on the underlying SnS. We observe that the alloy film gradually transforms from orthorhombic to cubic phase as calcium content increases. Electrical measurements show resistivity increases with calcium content in the alloy films, demonstrating tunable electrical properties with composition. After high temperature annealing, the cubic alloy film undergoes phase transition into orthorhombic and its resistivity also decreases, both of which agree with phenomena caused by phase separation of a metastable material upon addition of external energy.

4.3 Buffer layers with aluminum and indium doping

The p-n junction is essential in generating the photovoltaic behavior of a solar cell. The n-type layer (buffer) needs be well matched to the absorber in terms of its electronic band positions and carrier transport properties. It has been well demonstrated that tunable buffer layers can be obtained by adjusting the O/S ration in Zn(O,S). However, the O/S ratio also has a significant impact on the film carrier concentration and mobility. Both the band position and carrier concentration are essential factors in determining the efficiency of a solar cell, as shown in the modeling work in [86], and it is hard to optimize the entire solar cell with the codependency in band position and carrier concentration of the Zn(O,S) buffer layer. Therefore, we experimented with incorporating aluminum or indium into the Zn(O,S) buffer layer as an n-type dopant, so that the carrier concentration can be adjusted independently from the band position.

Continuing the work by Dr. Helen Park,[103] where she studied the effect of incorporating certain amount of Al in Zn(O,S) films with different O/S ratio,⁴⁹ I systematically studied the effect of Al content in the Zn(O,S) film with the same O/S ratio. The ALD dosing ratio of [DEZ/H₂O]:[DEZ/H₂S] = 7:1 was used to deposit the Zn(O,S) film, and one, two, three or four cycles of TMA/H₂O were added into a Zn(O,S) super cycle ([DEZ/H₂O]₇ + [DEZ/H₂S]₁). XPS analysis shows that the films are all carbon free and has a composition of S/(Zn+Al) = 0.20 ± 0.02,⁵⁰ and the Al content varies between 0 – 7%.⁵¹

100 nm of Zn(O,S):Al films were obtained by ALD and Hall measurement was conducted on them to measure the carrier concentration and mobility, which was presented in figure 4.5. We see that Al did not serve as meaningful n-type dopant as we intended but decreased the carrier mobility as its content increased up to 5%. When the Al content further increase to 7%, the carrier concentration is noticeably decreased, and the measurement become less reliable due to the high film resistance. One explanation is that the size of Al is too small compared to Zn and thus cannot fit well into the lattice or contributes free electrons to the conduction band. It is also possible that insulting Al₂O₃ clusters form as Al content increases, which can result in the observed increase in resistivity, especially at high Al concentration.

⁴⁹ In Helen's study, one TMA/H₂O ALD cycle were added to every other Zn(O,S) super cycle ([DEZ/H₂O]_m + [DEZ/H₂S]_n) and the O/S ratio was varied by changing m and n.

⁵⁰ Note that preferential sputtering of S is also an issue here, and it has been observed often that the O/S ratio increases with sputtering time. The composition reported here are from samples taken after 10 – 30s of Ar sputtering which was used to remove surface contaminants. No particular trend was observed for the S/(Zn+Al) ratio with the change in Al content.

⁵¹ Note that the XPS quantification is not very accurate for elements with low concentrations (<5%). It shows presence, and the trend shown by the scans is more trustworthy than the actual number of atomic concentration.

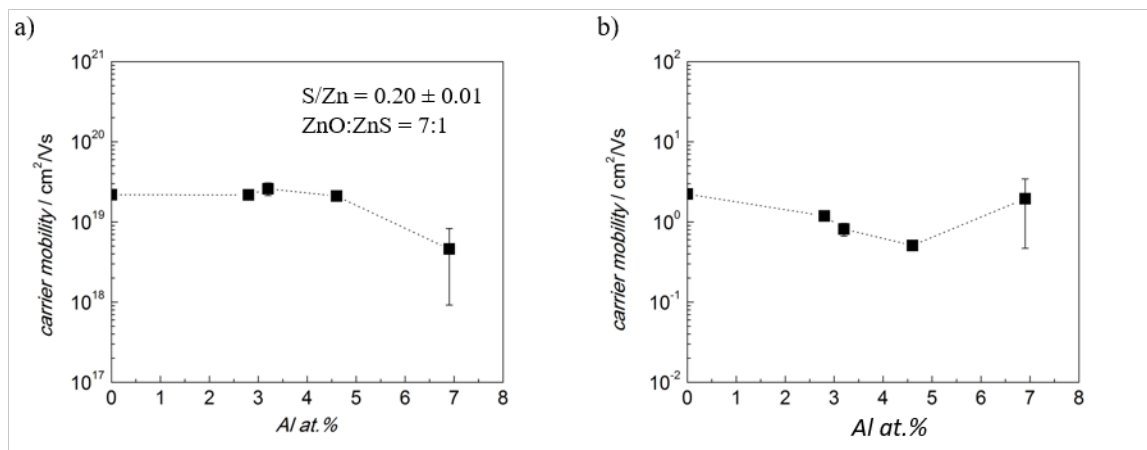


Figure 4.5 Carrier concentration (a) and mobility (b) of Zn(O,S) with different Al content.

Thus, we tried indium as an alternative dopant because of its comparable size to zinc. Indium was incorporated into the Zn(O,S) using the similar ALD processes as for Aluminum, and we used In(acac)₃ and water as the precursor. Presence of carbon was found in all Zn(O,S):In films, and Hall measurement again shows significantly increased film resistivity as In is incorporated. It worth noting that the reason for the unsuccessful In doping is different from that for the Al doping, and in the future, we may try a different In precursor that can give less C in the film.

4.4 Improving solar cell efficiency by adding an MgF₂ anti-reflection coating

While the ALD process is excellent in giving high quality and conformal thin films, it at the same time results highly reflective SnS films due to the relative good surface smoothness. Despite the successive Zn(O,S):N buffer and ITO window layers, our finished solar cell is still highly reflective, which, unsurprisingly, would leads to current loss. Therefore, we explore adding an anti-reflection coating (ARC) layer on top of our solar cells to improve the efficiency.

Anti-reflection coating (ARC) is a thin layer of dielectric material, with a specific thickness so that the wave reflected from the ARC top surface interferes destructively with the

wave reflected from the semiconductor surfaces, resulting in zero net reflected energy. We can calculate the optimal ARC thickness for this destructive interference by $d = \lambda/4n_1$, where λ is the wavelength that we want to minimize the reflection of, and n_1 is the refractive index of the ARC material. Reflection can be further minimized if the refractive index of the anti-reflection coating is the geometric mean of that of the materials on either side ($n_1^2 = n_0 n_2$). Therefore, for our air/ITO interface, 100 nm of MgF_2 ($n = 1.38$) selected as the ARC as the last step onto our solar cell fabrication.⁵² The MgF_2 ACR was sputtered using an RF gun of 150 W from an MgF_2 target, and under an Ar pressure of 4 mtorr for 180 min.

Figure 4.6 shows that the sputtered MgF_2 has small crystallites and strong charging effects in SEM compared to the ITO surface, which is the top-most layer for the control solar cell. The film composition was analyzed using XPS and the result presented in figure 4.7. The film contains small amount of C and O, and is slightly Mg-rich, which is not uncommon in sputtered ARC without additional F compensation. The ellipsometry data can be well fitted with existing model for MgF_2 , and the refractive index was extracted to be ca. 1.38, which agrees well with literature values. The resulting film thickness is 128 ± 5 nm as measured by both Ellipsometry and cross-section SEM.

⁵² For photovoltaic applications, refractive index and thickness are usually chosen in order to minimize reflection for a wavelength of 0.6 μm , because it is close to the peak power of the solar spectrum.

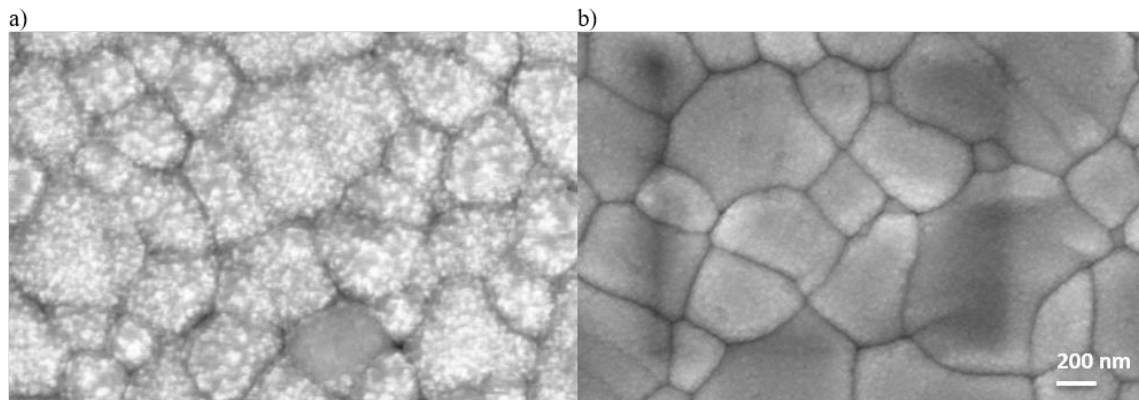


Figure 4.6 SEM images of a solar cell surface (a) with and (b) without the MgF_2 layer.

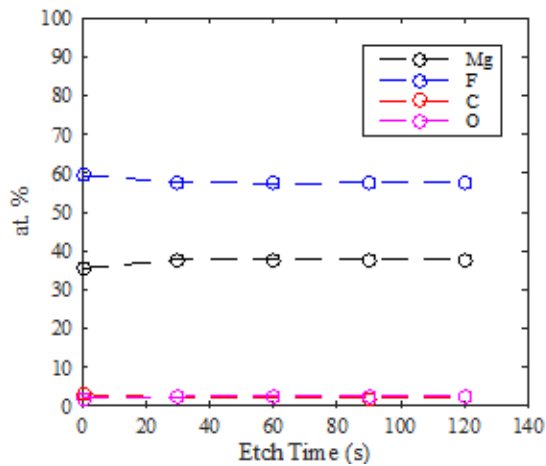


Figure 4.7 Composition of the sputtered MgF_2 film.

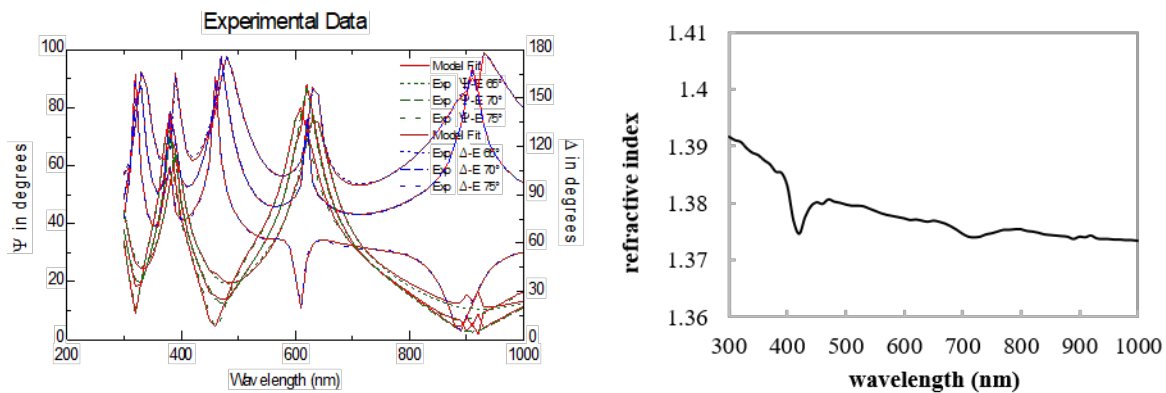


Figure 4.8 Ellipsometry results of MgF_2 . (a) Experimental and model fit for the Ψ and Δ values. (b) fitted refractive index.

The addition of MgF_2 leads to noticeable improvement in the solar cell performance, especially short-circuit current. As expected from the effect of ARC, the half of the cells coated with MgF_2 shows visibly lower reflectance compared to the half without MgF_2 as shown in figure 4.9. Figure 4.10 shows the IV and QE measurement of a cell measured before and after adding the ARC layer, which is 4.61% and 5.17% respectively. The short circuit current is improved from 22.3 to 26.0 mA/cm^2 , which is an impressive 16.6% increase.⁵³ The quantum efficiency, as shown in figure 4.8b, shows improvement between 580 nm to 700 nm, consistent with the effect of the ARC. The highest efficiency obtained for cells with MgF_2 is 5.22%, which is 7% higher compared to the previous 4.88% without MgF_2 , which sets a new record for SnS solar cells.

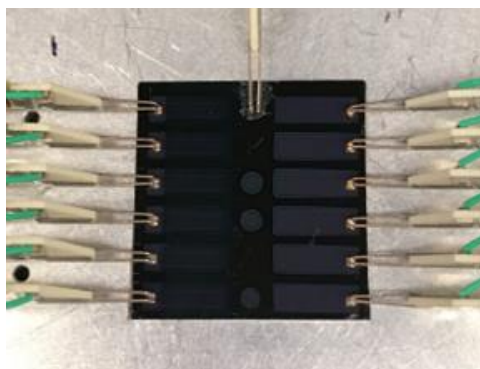


Figure 4.9 Photo of a batch solar cell with (left) and without (right) MgF_2 coating.

⁵³ This value is adjusted for the solar-simulator intensity variation during the year these measurements were taken. The actual J_{SC} measured was a higher value of 28.0 mA/cm^2 .

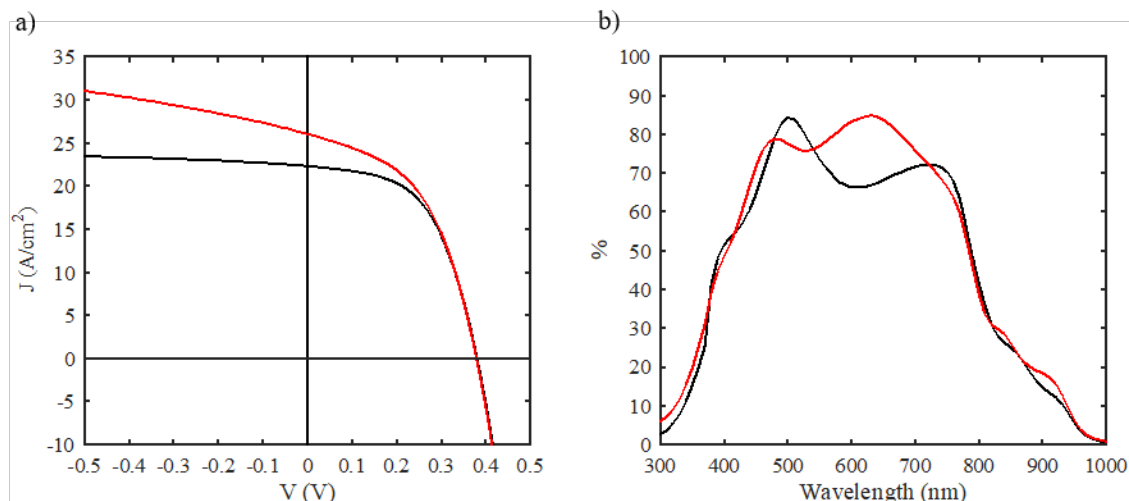


Figure 4.10 JV and QE measurements of a solar cell before and after MgF₂ coating. Black: no MgF₂. Red: with MgF₂.

Note that the fill factor was lowered due to the lower shunt resistance possibly caused by the pressure applied for masking the cell during MgF₂ deposition. Also, the MgF₂ used in this experiment is slightly thicker than the optimal value calculated, and the film deposited on glass under the same conditions looks a tint of grey to the eye, indicating absorption in the visible light range, which is also non-ideal for the solar cell. Thus, a few low-hanging fruits for further improving the solar cell efficiency can be picked by: more careful masking of the cell during MgF₂ deposition, decreasing the thickness, and optimizing the deposition recipe to improve optical transmission.

4.5 Conclusion and future work

In conclusion, we deposited SnS thin films using ALD, studied the reaction mechanisms and crystal structures, systematically investigated the major components of the solar cell, and improved the record solar cell efficiency to 5.2%. We proposed a modified ALD mechanism for reaction between of the new liquid Sn precursor with H₂S, where both ligands of Sn precursor

molecule can react with surface thiol groups upon the Sn exposure step of ALD, with the presence of other chemisorption mechanisms such as dissociation and association. The crystallographic phases and orientations of SnS were found to change with temperature, film thickness, and substrate. We demonstrated that highly oriented SnS can be achieved using a NaCl (100) substrate, and device can be fabricated by dissolving the NaCl. We also studied the back contact, buffer layer, ARC, and explored alternatives for making the absorber by alloying with CaS or by conversion from SnO.

For future studies, one can further optimize the deposition conditions to obtain phase-pure epitaxial or preferably orientated SnS films to achieve better carrier transport properties through the solar cells absorber. The electrical properties, the bandgap and absorption coefficient, the photo-luminescent responses, and the minority carrier lifetimes of the newly resolved π -SnS are areas for more characterizations. Also, it is worthwhile to improve the device fabrication process for the SnS grown on NaCl, where cell performance can benefit from higher qualities of contacts and higher device yield. In addition, there is a high possibility of further boosting the device efficiency by optimizing the MgF₂ deposition methods to achieve a better ARC layer.

Another interesting direction would be to study the SnO film, which has been demonstrated to be a p-type semiconductor but has not been studied much. It might be interesting to characterize the ALD behavior of SnO and to explore its applications as an electronic component or continue to study its conversion to SnS.

Lastly, one may conduct more thorough mechanistic and crystal structure studies in the context of SnO and SnS and, as a long shot, propose a theory to relate the reaction mechanism of the ALD process to the microstructure of the deposited material.

Appendix A Summary of major SnS literature

Table A.1 SnS literature using vapor deposition methods organized by author and year of publication.

Ref.	T (°C)	d (nm)	Phase	Prefer. Orient.	E _g (eV)	R (Ω·cm)	p (cm ⁻³)	μ (cm ² /Vs)	Others
[1] [7]	960	20000	bulk α, β	-	1.08, indirect ⁵⁴	-	10 ¹⁷ – 10 ¹⁸	65 - 90	μ _c /μ _b = 5.5 μ _c /μ _a = 1.15 note ⁵⁵
[33]	-	-	thin film zb ⁵⁶ , hex	-	-	-	-	-	1 st report of cubic SnS
[34]	25 – 150	100	thin film rs	-	-	-	-	-	NaCl
[35]	400 – 500	-	thin film rs	-	-	-	-	-	NaCl
[9] [10]	700	-	bulk α, β	-	-	-	-	-	-
[26]	150 – 350	-	thin film α + Sn _x S _y	(111) → (040) as T↑ ⁵⁷	1.48, direct	13 – 20	6.3×10 ¹⁴ – 1.2×10 ¹⁵	400 – 500	PV 0.29% note ⁵⁸
[36]	200 – 450	~1000	thin film α + Sn _x S _y	(111)	1.3 direct	-	-	-	note ⁵⁹
[37] [38]	50 – 325 (275)	500	thin film α + Sn _x S _y ?	(111) → (040) as d↑ ⁶⁰	1.35 direct	30 – 200	-	-	ε = 12.41 n ₀ = 3.52 note ⁶¹

⁵⁴ Good linearity fit. Bandgap decreases with temperature. At T = 77K, E_{g,ind} = 1.115 eV.

⁵⁵ Experimental anisotropic electrical properties: μ_c/μ_b = 5.5 ± 0.5, μ_c/μ_a = 1.15 ± 0.1 at room temperature. Experimental temperature dependence: μ decreases with temperature for T > 50K and decrease as T^{-2.2} in the range 200 – 600 K (μ = 20 – 1000 cm²/Vs in the temperature range of 600 – 20K); p increases with temperature.

⁵⁶ Abbreviations: zb: zinc-blende; rs: rock-salt; hex: hexagonal; tet: tetragonal

⁵⁷ Also seen is preferred orientation dependence on substrates.

⁵⁸ Film is 10% S-rich from XRF and AES, even starting source is pure (4N) SnS powder. Author inferred from the large optical bandgap that the film contains secondary phases of Sn₂S₃ and SnS₂.

⁵⁹ Film made from co-evaporation of Sn and S. Conducted parameter study to deposit pure SnS. Film composition and phases (SnS vs. SnS₂) are controlled by substrate temperature and rate of evaporation of Sn and S. I don't think there is enough data to support they have phase purity for the films they claim to be SnS.

⁶⁰ The resolution of the XRD was a bit questionable. Orientation dependence on substrate is: (040) dominates on Si, while (111) on glass, Ag, ITO, etc. Also, there is no peak at (080) position, confirming that the peak is indeed (111). The (111) → (040) transition happens when thickness past 750nm.

Table A.1 (Continued) SnS literature using vapor deposition methods organized by author and year of publication.

Ref.	T (°C)	d (nm)	Phase	Prefer. Orient.	E _g (eV)	R (Ω·cm)	p (cm ⁻³)	μ (cm ² /Vs)	Others
[39]	300	500	thin film α	(040) ⁶²	1.47 direct	-	-	-	Slightly Sn-rich
[40] [42]	210 – 350	500 – 8000	thin film α	(111) → (040) as T↑ ⁶³	1.07 – 1.27 direct	-	-	-	Slightly Sn-rich
[59]	25	230 – 1600	thin film α + π? ⁶⁴	(111) → (002) as P _{Ar} ↓	1.08 – 1.18 indirect	1100 – 97000	-	-	RF-sputter Slightly Sn-rich
[41]	700	750 – 1140	powder doubtful XRD	-	1.06 – 1.32 indirect	-	-	-	-
[44]	280 – 360	~5000	thin film α	(111) → (040) as T↑ ⁶⁵	1.30 – 1.34 direct ⁶⁶	-	-	-	L _n = 230 nm n = 5.2 – 5.9
[13]	300 – 500	200 – 400	thin film -	-	1.07 indirect ⁶⁷	-	3×10 ¹⁴ – 1×10 ¹⁶	4 – 16	PLD note ⁶⁸

⁶¹ Conducted parameter study to deposit pure SnS by controlling temperature. S content decreases from Sn/S = 0.9 to 1.1 as T increase from 50 to 350°C. But doubtful XRD assignment of SnS₂ peaks at low temperatures; n_{avg} = 2.05.

⁶² XRD was not well aligned, but the assignment should be correct since the (080) peak can also be seen.

⁶³ Transition happens around 230°C on glass substrate, but film maintained (111) domination for all thickness and all temperature on Mo coated glass substrate → substrate dependence of orientation. Lower temperature, thinner films and Mo surface were seen to lead to more polycrystallinity/less texturing.

⁶⁴ Katy sputtered SnS in a range of Ar pressure at room temperatures and found prominent peaks at 30.9° when using high Ar pressures, which she doubtfully assigned to Sn₂S₃ despite the stoichiometry shows the films were slightly Sn-rich. In hindsight, it is possibly that that peak belongs to cubic SnS.

⁶⁵ More polycrystalline at lower temperatures, more prominent (110) (120) (021) peaks at 280°C, while (040) clearly dominates at 360°C.

⁶⁶ Linearity fit not shown. Bandgap decreases slightly with temperature increase.

⁶⁷ Also calculated and compared to measurement of ~1.5eV absorption onset.

⁶⁸ Hole concentration decreases with temperature.

Table A.1 (Continued) SnS literature using vapor deposition methods organized by author and year of publication.

Ref.	T (°C)	d (nm)	Phase	Prefer. Orient.	E _g (eV)	R (Ω·cm)	p (cm ⁻³)	μ (cm ² /Vs)	Others
[61]	100 – 400	~1000	thin film α	(040) at high T; epitaxial: graphene	0.98 indirect 1.21 direct	-	1×10 ¹⁶ – 6×10 ¹⁷ (doped)	81	MBE
[62]	300	300	thin film α	(040)	1.45 direct	500	2.8×10 ¹⁶	-	anneal TE Sn-S; E _a = 0.06 eV
[45]	270 – 350	200	thin film α	(111) → (040) as T↑ ⁶⁹	1.91 – 2.01 direct	95 – 335	-	-	Sn-rich as T↑ note ⁷⁰
[46]	85 – 325	100 – 1200	thin film α	(111)/(040) at high T ⁷¹	1.14 – 2.3 direct ⁷²	-	-	-	S-rich
[47]	60 – 250	1500	thin film α	(120) & (021) ↑ as T↑ ⁷³	-	-	-	-	PV 1.6%
[48]	365	600	thin film α	(040) epitaxy ⁷⁴	1.0 indirect 2.3 direct	-	~10 ¹⁷	385	NaCl (100) n = 4.2
[57]	300 – 600	150	thin film α	(040) w/ (120) epitaxy	1.08 indirect	-	4×10 ¹⁴	25 – 37	PLD; MgO (100) E _a = 0.15 eV note ⁷⁵

⁶⁹ Also cited is that deposition speed also influence orientation (fast 111 slow 040).

⁷⁰ Tetragonal beta phase SnS at 410 °C with (a=c=0.3 and b=1.151 nm).

⁷¹ The author assigned dominate peak at high temperature at 31.7 to (111) → I suspect it should be (040) given the (080) peak also showed up. The author also assigned a few other peaks to Sn₂S₃ & SnS₂ that appear doubtful to me.

⁷² Doubtful linearity fit. But the trend is that bandgap decrease as thickness or temperature increase.

⁷³ The (111)→(040) transition with T might be shadowed by the overlapping ZnO substrate peaks. π-SnS not seen.

⁷⁴ Confirmed with TEM & pole figure

⁷⁵ Also measured are E_{Boundary} = 0.05 eV → μ₀ = 200

Table A.1 (Continued) SnS literature using vapor deposition methods organized by author and year of publication.

Ref.	T (°C)	d (nm)	Phase	Prefer. Orient.	E _g (eV)	R (Ω·cm)	p (cm ⁻³)	μ (cm ² /Vs)	Others
[60]	100 – 300	200	thin film α	(111) or (040) note ⁷⁶	1.57 – 1.77 direct ⁷⁷	-	-	-	EE + anneal
[50]	150 – 350	-	thin film α + Sn ₂ S ₃ & SnS ₂	(111) or (040) note ⁷⁸	1.24 forbidden direct ⁷⁹	10 ³ – 10 ⁵	-	-	Sn-rich n = 3.0 – 3.3
[30]	240 400 ^{annl} l	~1000	thin film α		-	-	-	-	PV 3.88%
[58]	25 200 – 600 ^{annl} l	150	thin film α	(111) → (040) as T _{annl} ↑	1.05 – 1.1 indirect	-	1.5×10 ¹⁵ 1.6×10 ¹⁶ (annl)	2 28 (annl)	TFT; S-lost at high T
[24]	250 – 350	240 – 300	thin film α + π π → α as T ↑	(111) → (040) as T ↑ note ⁸⁰	1.1 indirect 1.3 – 1.4 direct ⁸¹				
[87]	950	-	bulk α	(111) or (040)	1.3/1.78 direct	-	5×10 ¹³ – 2×10 ¹⁷	-	S-rich τ > 3 ns (PL)
[79]	600 – 700	-	nanowire cubic a= 0.55 Å	grow along (100)	-	-	6.3×10 ¹⁸	0.015	CVD-Au Sn-rich FET

⁷⁶ Doubtful assignment. Only one peak near (111) was shown in XRD, and the XRD has pretty low resolution. The peak at high temperature was likely to be (040) since the (080) peak was clearly present.

⁷⁷ Doubtful linearity fit. But the trend is that bandgap decrease as temperature increase.

⁷⁸ Doubtful assignment. There likely exist a (111) → (040) transition as T increase, given that the (080) peak appeared as T increase.

⁷⁹ Okay linearity fit. Author shows that bandgap increase with temperature, which contradict other findings.

⁸⁰ At T<300°C, the film consists of mixed α and π phase, and π phase decrease with temperature increase.

The dominating peak at high temperature was assigned (111), but I think it is more likely to be (040).

⁸¹ Okay linearity fit for both. Bandgap decrease as T increase.

Table A.2 SnS literature using atomic layer deposition organized by author and year of publication.

Ref.	T (°C)	d (nm) / g.r. ⁸²	Phase	Prefer. Orient.	E _g (eV)	R (Ω·cm)	p (cm ⁻³)	μ (cm ² /Vs)	Others
[51]	175	23 / 0.46	-	-	1.87 direct	-	-	-	Sn(acac) ₂ H ₂ S
[28]	100 –	97 –	α	(040) →	1.3 –	60 – 700	7×10 ¹⁵ –	0.82 –	Sn(A- amd) ₂
[29]	250	370 /		(111) as	1.43		1.6×10 ¹⁶	15.3	H ₂ S
[52]		0.9		d↑ ⁸³	direct				PV 4.4%
[53]	60 – 180	50 / 0.35 – 1.67	amorph. → α as T↑ ⁸⁴	(111) & (120)	1.10 – 2.76	~ 100	-	-	TDMA Sn H ₂ S note ⁸⁵
[54]	300	4.5 / 0.47	α	-	-	-	-	818	Sn(acac) ₂ H ₂ S +WS ₂
[55]	90 – 240	< 30 / 0.45– 0.07	π + α π → α as T↑	(040) & GIXRD ⁸⁶	1.45 direct	-	-	2.9	Sn(dmam p) ₂ H ₂ S TFT
[23]	80 – 175	< 80 / 0.40	π → α as T↑ ⁸⁷ α → π as H ₂ S↑	GIXRD ⁸⁸	1.64 forb. direct ⁸⁹	-	-	-	Sn(acac) ₂ H ₂ S S-rich note ⁹⁰
[56]	200 400 ^{ann} 1	500 / -	α	(040) Au (111) Mo/ Ti	-	50 – 500	-	-	Sn(A- amd) ₂

⁸² g.r. denotes growth rate in Å/c

⁸³ Also increases with thickness is the peaks (101) (120) and (002). Small cubic (111) observed at for films deposited at 120 °C.

⁸⁴ Below 120 °C, SnS_x films appeared to be amorphous. SnS_x films were SnS₂ hexagonal at 140 °C and 150 °C and SnS orthorhombic above 160 °C.

⁸⁵ Work function_{UPS} = 4.44_{100C} – 4.64_{180C} eV; Binding energy_{UPS} = 4.68_{100C} – 4.03_{180C} eV. This put Fermi at mid-gap and n-type (or possibly caused by surface O).

⁸⁶ XRD shows no peak below 150 °C and (040) peak only above 210 °C.

⁸⁷ The π-peaks still clear up to 175 °C /40nm.

⁸⁸ For 80nm film deposited at 120 °C, the π phase was only apparent when the angle of GIXRD increase.

⁸⁹ Refractive index of π- and α- SnS are measured: n_{inf,pi} = 3.4 n_{inf,ortho} = 3.2.

⁹⁰ RBS show up to 15% S-rich, and film density was measured to be 4.5, lower than bulk density. GIXRD and Raman show no Sn₂S₃ & SnS₂.

Table A.3 SnS literature using solution-processing methods organized by author and year of publication.

Ref.	T (°C)	d (nm)	Phase	Prefer. Orient.	E _g (eV)	R (Ω·cm)	p (cm ⁻³)	μ (cm ² /Vs)	Others
[64]	25 – 75	~ 1000	-	-	-	10 ⁴ – 10 ⁵	-	-	photo current
[27]	350	600	thin film α	(111) ⁹¹	1.32, direct	23	-	-	Spray-pyr. PV 1.33%
[75]	170 – 300 250 – 300 ^{ann}	-	nanopar. zb (π?); ⁹² zb → α as T _{dep} ↑	-	α: 1.05 zb: 1.5	-	-	-	zb: tetrahedra α: platelet note ⁹³
[78]	70	50	nanodisk α	(040)	-	-	-	-	epitaxy on Au (100) ⁹⁴
[65]	-	-	thin film zb	-	-	-	-	-	a = 0.5783 Å
[66] [71]	7 – vary	-	thin film zb (π?) ⁹⁵ α	-	zb: 1.71 fb. direct α: 1.15 indirect	zb: 10 ³ – 10 ⁶ α: 400	-	-	SILAR note ⁹⁶
[77]	210 – 280	-	nanopar. α	all	-	-	-	-	needles & plates
[74]	200 – 280	8 – 700	nanopar. α + zb + SnO ₂ (π?) ⁹⁷	all	1.65 – 1.68 direct	-	-	-	truncate tetrahedra 5.845 Å
[67]	60 – 80	350 – 450	thin film α	(111) (101)	1 – 1.26 indirect	10 ² – 10 ³	-	-	note ⁹⁸

⁹¹ XRD resolution was low, the single-dominating peak could be (040).

⁹² XRD spectra show characteristic π-triple peak, and TEM and SAED patterns cleanly show cubic symmetry. But author conclude ZB-SnS with impurities (a = 5.845 Å)

⁹³ The zb/π tetrahedral was stable when annealed at 300°C in Ar but converted to α in oleylamine.

⁹⁴ Beside XRD, the authors also have pole figure, rocking curve, and azimuthal scan to support the epitaxy claim. But SEM morphology shows nanodisk projecting out of the plane.

⁹⁵ Poor XRD resolution, yet clearly see peaks at 26.7 and 30.9 and can vaguely see the π-triple peaks.

⁹⁶ Both temperature and pH determine the phase. Also discussed by the authors are the deposition mechanisms: ion-by-ion for ZB and hydroxide cluster for the α-SnS.

⁹⁷ However the pattern corresponds to quite clean π-phase (the characteristic π-triple peak) for crystals of all size, and TEM show cubic symmetry and tetrahedral crystallites that support cubic assignment.

⁹⁸ The (101) peak was shifted and likely can be assigned to π-(400), yet there's no other major π peaks, but clear α-(131) and (002) peaks. Morphology also doesn't show any tetrahedral → film is indeed α.

Table A.3 (Continued) SnS literature using solution-processing methods organized by author and year of publication.

Ref.	T (°C)	d (nm)	Phase	Prefer. Orient.	E _g (eV)	R (Ω·cm)	p (cm ⁻³)	μ (cm ² /Vs)	Others
[76]	170	~100 ×500 ×11000	nanobelt	(040)					Li-ion battery
[73]	140 – 180	10 – 300	nanopar. tet. α	-	-	-	-	-	proposed a tetragonal phase ⁹⁹
[18]	14 – 70	230 – 600	thin film zb/π, α	GIXRD	π ~ 1.7, for.	π ~ 10 ⁶ – 10 ⁷	-	-	PV ¹⁰⁰
[22]	350 – 400 ^{anl}		zb/π → α as T _{dep} ↑		direct; α ~ 1.1, indirect	α ~ 10 ³ – 10 ⁴			1.28% 0.5794 Å Anneal → stable π ¹⁰¹
[16]	140 – 240	20 – 100	nano par π, α	π – (111)	π ~ 1.53, indirect; α ~ 1.10, indirect	-	-	-	tetrahedra note ¹⁰³
[19]			π → α as T ↑	facet note ¹⁰²					
[20]									
[21]	25 – 65	450 – 800	thin film π	all	1.68 – 1.74, direct	10 ⁴ – 10 ⁵	10 ¹² – 10 ¹³	6 – 75 ¹⁰⁴	Sn-rich ¹⁰⁵ Anneal → unstable π ¹⁰⁶
[69]	150 – 350 ^{anl}								

⁹⁹ The authors proposed a tetragonal phase to so that the often observed “mixed zb+α phases” can be consolidated in a single phase. But the XRD and TEM characterizations did not give enough evidence and the tetragonal phase have higher formation energy, so the π phase seems a more likely solution.

¹⁰⁰ V_{OC} = 0.47 V, J_{SC} = 6.2 mA/cm², τ ~ 2 – 20 ns, R_s = 23 Ω. V_{OC,16sun} = 0.6 V, J_{SC,16sun} = 35 mA/cm².

¹⁰¹ XRD pattern for the π-SnS film did not change after annealing at 400°C in N₂. → a stable phase!

¹⁰² Authors explained the formation of the π phase as: the interaction at the surface between the growing nanocrystal and the capping agent determines the energetically favorable crystal facet. Under specific conditions, this favorable facet corresponds to the cubic phase, leading to the formation of π-SnS. They hypothesize that π-SnS is a kinetically accessible phase and an energy barrier prevents its immediate transformation into α-SnS. The phase ratio is affected primarily by the capping agent composition.

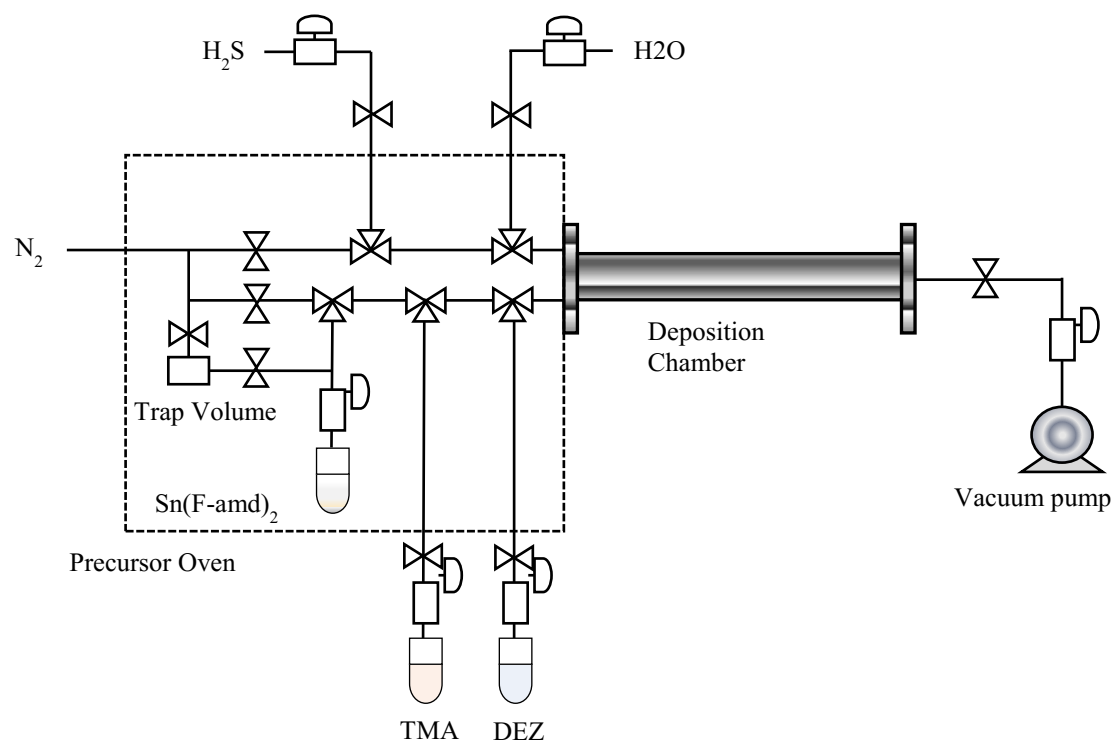
¹⁰³ DFT simulation: m_{h,v,pi} = 1.22 m₀, m_{e,c,pi} = 0.76 m₀, m_{h,v,orth} = 0.31 m₀, m_{e,c,orth} = 0.15 m₀

¹⁰⁴ Except one outlier sample at 25 °C showing μ = 0.68 and p = 10¹⁵.

¹⁰⁵ The films are Sn-rich film up to Sn₂S and seems to contain O (possibly in the form of SnO_x or SO₄²⁻). But the XRD peaks corresponds well to π-SnS, and Raman peaks at 90 and 109 cm⁻¹ also indicate π-SnS.

¹⁰⁶ Annealing at T = 150 °C for 10min still result in pi-SnS, with improved grain size, but annealing at T > 250 °C produce SnS₂ and change morphology from round-like to flake-like.

Appendix B Diagram of the ALD reactor



⋈ 2-way control valve

⋈ 3-way control valve

□ Manual valve

Appendix C QCM Supplementary Information

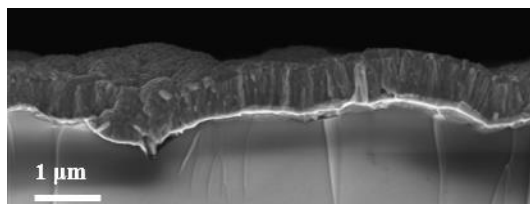


Figure C.1 Cross-sectional SEM image of SnS deposited on Mo covered QCM crystal. The surface roughness of the quartz-crystal can lead to higher than expected readings of ng/cm² from the QCM.

Appendix D XPS study of Ar-sputtering damage of SnS

We can see from figure D.1a that the higher the sputtering voltage, the more the Sn^0 peak, indicating more reduction of the Sn^{2+} and loss of S using high sputtering voltages. Figure D.2b shows that the time of sputtering is not essential beyond the initial removal of surface species.

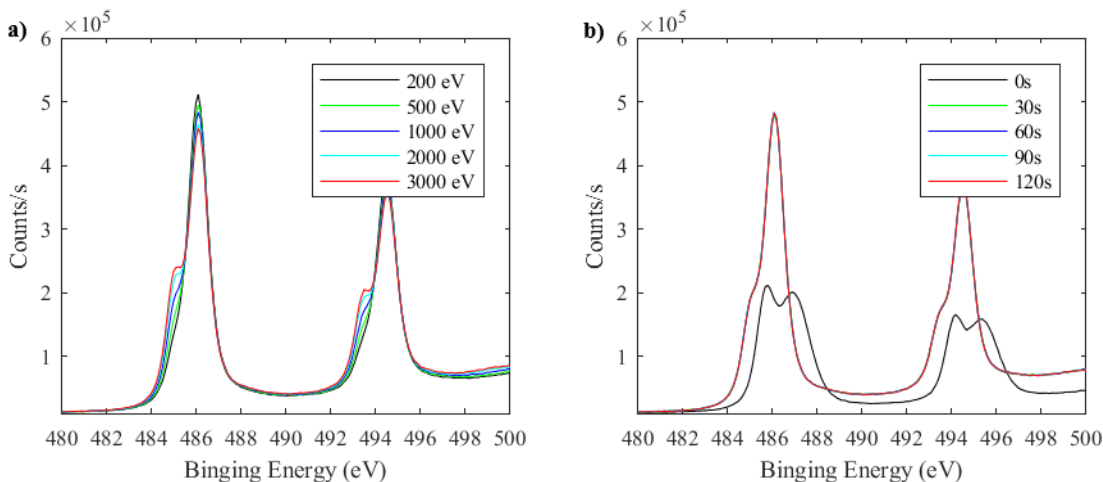


Figure D.1 XPS Sn 3d scans under (a) 60 s of Ar-sputtering using 200 – 3000 eV, and (b) 0 – 120 s of Ar-sputtering using 1000 eV.

Appendix E Solar cell fabrication from SnS deposited on NaCl

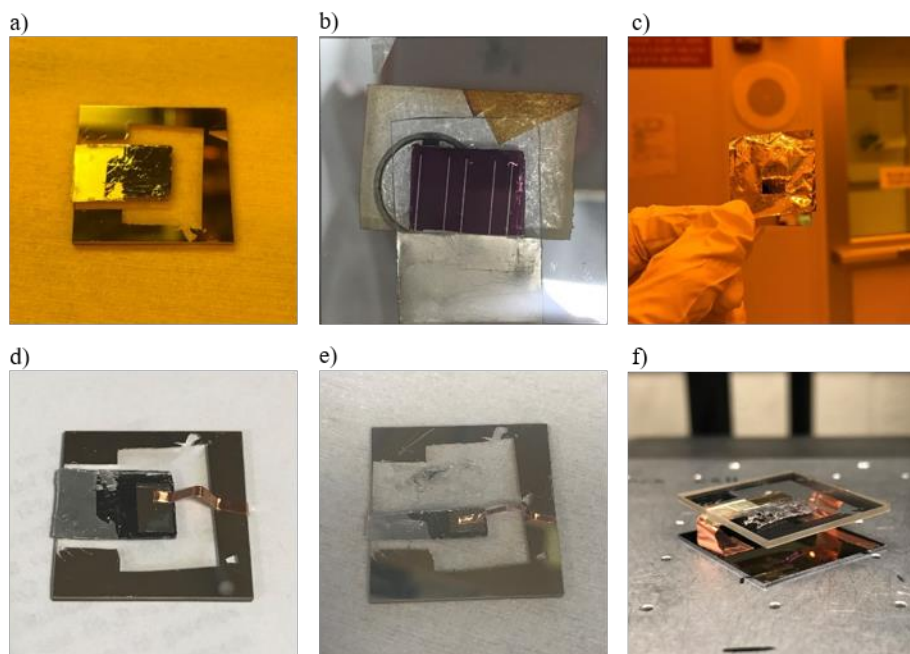


Figure E.1 Processing photos during the solar cell fabrication from NaCl substrate.

Another fabrication method used is to make the solar cell in a substrate configuration, where the supporting piece during the substrate dissolving step will eventually be removed. Photoresist was coated to the NaCl – SnS – Buffer – Window – Ag figure device stack to provide a mechanical support during the later lift-off. The detailed process can be found in figure E.2a-e. The spin-coating procedure caused most of the film to be destroyed, as shown in figure E.1f. Only the film in the left 1/5 of the sample seemed intact to the eye, and the spin-coated photoresist was too thin to form a support – film was very fragile and curved due to stress, and it later cracked to small pieces when I tried to pick it out by tweezers. For future reference, one should just drop cast the photoresist to the sample and let dry by soft baking.

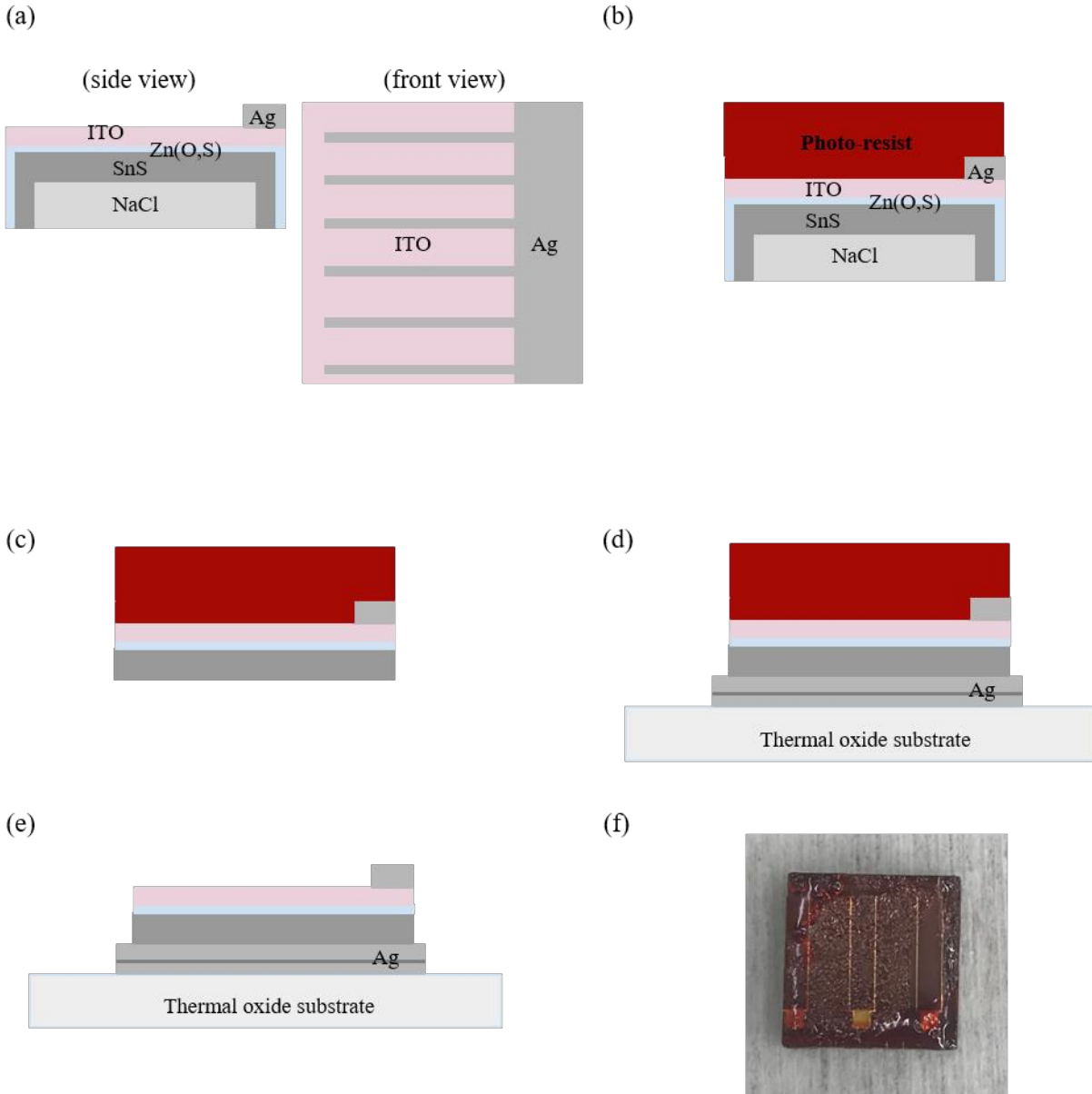


Figure E.2 Fabrication scheme 1 – the superstrate configuration. (a) The starting device stack on NaCl fabricated using the regular methods. (b) Apply the photo-resist – use drop cast, do not spin coat. (c) dissolving the NaCl substrate in water. (d) Evaporate Ag on the back contact and on a silicon thermal oxide substrate; then put the sample on the substrate with their Ag-side facing each other and apply pressure and vacuum for better bonding between the Ag-surfaces. (e) Dissolve the photoresist in acetone. (f) A photo of the device after step (b).

Appendix F Reference XRD peak tables

Table F.1 Reference XRD peak tables of π -SnS α -SnS, rock-salt SnS and NaCl.

π -SnS ¹⁰⁷		α -SnS (PDF_00-039-0354)		rs-SnS (PDF_01-077-3356)	
2 θ (°)	hkl	2 θ (°)	hkl	2 θ (°)	hkl
23.01	300	22.011	110	26.598	111
26.63	222	26.01	120	30.808	200
27.74	320	27.473	21	44.128	220
28.81	321	30.474	101	52.269	311
30.84	400	31.532	111	54.783	222
31.82	410	31.972	40	64.179	400
32.76	411	39.046	131	70.747	331
34.59	420	39.33	41	72.875	420
35.47	421	41.685	200	81.179	422
39.63	510	42.507	210	NaCl (PDF_05-0628)	
40.42	511	44.74	141	2 θ (°)	hkl
44.18	440	45.496	2	27.335	111
44.9	441	48.511	211	31.693	200
50.39	540	51.088	112	45.450	220
51.04	541	51.313	151	53.854	311
52.33	622	53.148	122	56.479	222
52.97	542	53.443	160	66.229	400
54.85	444	54.073	231	73.066	331
55.47	700	54.257	61	75.304	420
56.08	710	56.676	42	83.973	422

¹⁰⁷ Simulated 2 θ peak positions from the crystallographic information files (CIF) reported in Rabkin, A., et al., *New nanocrystalline materials: a previously unknown simple cubic phase in the SnS binary system*. Nano Lett, 2015. 15(3): p. 2174-9

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