Purity Matters: Enhancing Carrier Transport Properties in Tin Sulfide for Photovoltaic Applications by Reducing Impurity Content

By
Alex J. Polizzotti

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Signature redacted

Signature of Author: ____________________________

Department of Mechanical Engineering
Sept 11, 2015

Certified by: ____________________________
Tonio Buonassisi
Associate Professor of Mechanical Engineering
Thesis Supervisor

Accepted by: ____________________________
Rohan Abeyaratne
Quentin Berg Professor of Mechanics
Chair, Committee for Graduate Students
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ABSTRACT
Tin sulfide (SnS), a potential p-type absorber material for photovoltaic applications, is hampered by poor carrier-transport properties, particularly minority-carrier lifetime. This study investigates the role of intrinsic and extrinsic crystallographic point defects on the electronic transport properties of SnS. High-purity SnS is grown via sulfurization of tin films, and compared with baseline material made from feedstock with two orders of magnitude higher impurity content. Minority-carrier lifetime, morphology, and impurity content are analyzed in both materials. It is shown that improving feedstock purity by two orders of magnitude results in an improvement to minority-carrier lifetime from under 100 ps to over 2 ns. Simulations suggest that this increase in minority-carrier lifetime could lead to device efficiency improvements.

Thesis Supervisor: Tonio Buonassisi
Title: Associate Professor of Mechanical Engineering
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Chapter 1
Introduction & Motivation

1.1 Introduction to photovoltaics

Solar photovoltaics (PV) has gained significant attention over the past several decades as a viable alternative energy source to fossil fuels. Several key strengths position solar as a sustainable and long-term global energy solution. The solar resource is free and highly abundant – up to 1000 W/m² of solar radiation is incident on the earth’s surface on a cloudless day at certain latitudes, with over 23,000 TW of total solar resource averaged over the year [1]. This is several orders of magnitude above human demands, which were estimated at 17.7 TW averaged over 2012 [2]. The generation of energy from this resource is carbon-cheap – solar panels have warranties of >25 years but energy payback times of only ~1-3 years depending on the specific technology [3] – meaning that if photovoltaics were deployed en masse it would reduce civilization’s carbon footprint and potentially avert the worst effects of anthropogenic climate change. Lastly, the cost of photovoltaic devices has dropped precipitously since their inception in 1955 at Bell Labs, and in fact recent predictions by Deutsche Bank show solar photovoltaics reaching grid parity in ~80% of the world within the next two years [4].

Until recently, the solar market has been dominated by PV devices made from high-purity silicon semiconducting wafers. Great strides have been made with silicon, and record device efficiencies of 25.6% have recently been achieved by Panasonic [5]. However silicon has limitations – it has a relatively low optical absorption coefficient (<10⁴ cm⁻¹ for most of the visible range) [6], meaning that it does not absorb light as well as many other materials. As a result, these devices require, at a minimum, several tens of microns of silicon to effectively absorb all solar photons, and thicker layers are often required for ease of handling and processing.

A thick layer of silicon means that electrons need to travel long distances in order to be extracted from the cell – i.e., the silicon used in these cells must have very good charge transport properties. Good charge transport requires extremely high-purity, near-perfect silicon crystals (or polycrystals). Such purity has its cost - many energy-intensive (and thus expensive) processing steps are needed to convert low-purity silicon oxide feedstock to high-purity silicon crystals. These two factors – the cost of creating high-purity silicon, and the need for thick layers of the material for each panel – result in ~1/3 of the entire silicon module price (approximately $0.35 per peak watt of PV output), being due solely to the cost of the silicon wafer [7].
The aforementioned challenges have generated interest in alternative materials to augment the burgeoning silicon PV market. In fact several materials (notably CdTe [8], and GaAs [9]) have achieved efficiencies > 20% and some market share of the PV industry. These so-called “thin film” materials were selected for their strong optical absorption coefficients, as well as other optical properties. As a result, very thin films on the micron scale or less are sufficient to absorb all incident solar radiation in these materials. These thin film absorbers hold the promise of low materials cost, partially because of this low materials requirement. Moreover, since electrons must only travel through a thin layer, these materials may not require purity and charge transport properties as high as that of silicon.

There are still minimum charge transport requirements that thin film absorbers must meet, however. As shown below, most thin film materials (with the exception of the few mentioned above) have stagnated at efficiencies below or barely above 10% despite careful selection of optical properties [10], [11]. Deeper improvements to thin film PV materials are necessary to fully capitalize on their many potential advantages. For this reason, along with the scale of production, scientific maturity, and innovative cell architectures used in silicon photovoltaics, silicon still dominates in the PV industry.

Figure 1.1: Thin film solar efficiencies. With few exceptions, emerging thin film materials show low efficiencies below 10%. This is despite careful selection for optical properties. Other material parameters must also be optimized to achieve high final device efficiencies. Figure reproduced from Steinmann et al, 2015 [10].
One of the main challenges for thin film PV is that while the community has screened for materials with good optical properties, these materials have not historically been screened for their charge transport properties. While thin film PV may not need transport properties on par with silicon, poor transport properties still limit many thin film materials [12]–[15]. In the course of this work, I will investigate a potential PV absorber material, tin sulfide, and attempt to improve its charge transport properties.

1.2 Tin sulfide for photovoltaic applications

Tin monosulfide (SnS) is characterized by several of the benefits of thin film absorbers mentioned above. It has a high absorption coefficient in excess of $10^6 \text{cm}^{-1}$ [16]. It has an indirect bandgap of 1.1 eV and direct transitions at 1.3 and 1.5 eV, meaning that it is tuned to absorb the highest-yield photons from the solar spectrum [17]. Its binary composition means that there are fewer potential atomic rearrangements (i.e., crystallographic imperfections) than a more complex ternary or quaternary material such as Cu(In,Ga)Se$_2$ or Cu$_2$ZnSnS$_4$ [18]–[20]. At moderate temperatures, SnS evaporates as a dimer, meaning that stoichiometric control via scalable processes such as thermal evaporation is simplified. Lastly, SnS is nontoxic and made solely of abundant elements [21] meaning that materials costs could potentially be low.

Efficiencies of devices made from SnS have risen sharply over the past several years. The first SnS PV devices with 1.3% device efficiency [16] were achieved in 2006. However since the beginning of a collaboration between the MIT PV lab and the Harvard Gordon group in 2011, record devices with a certified efficiency of 4.4% using SnS films deposited via atomic layer deposition [22] and 3.88% efficiency using thermally-evaporated SnS [23] were achieved in 2013 and 2014, respectively.

Unfortunately, certain drawbacks have inhibited further progress. As will be discussed in detail below, SnS grown by the above methods has been found to be limited by poor electronic transport properties – specifically low minority-carrier lifetimes of $<100 \text{ps}$ [15], [24]. Put simply, most electrons in SnS do not stay in an excited state long enough to be extracted for useful work.

During the course of this work, I aim to demonstrate that the low minority-carrier lifetime in SnS is due to impurities in the material. Further, I present a marked improvement in minority-carrier lifetime in materials grown from high-purity feedstock.
1.3 Bounds of this study

In this study I investigate the behavior of point defects in SnS, and how they affect electronic transport properties. I will show that the SnS grown for this study does not conform to prior theory of an ideal crystal (Kroeger-Vink modelling), in contrast to previously published work on SnS [25], [26]. This indicates that there is a more complex defect structure than this relatively simple model. I will show that this non-ideal behavior is likely to be explained by impurities in the material.

My hypotheses, therefore, are that

1) Poor carrier transport in the SnS I grow for this study is dominated by contamination both from impure feedstock material and during processing
2) Reducing contamination levels in SnS thin films by up to two orders of magnitude will result in an increase in carrier transport properties.

To test these hypotheses, I grow phase-pure SnS from feedstock that is two orders of magnitude cleaner than that traditionally used for our “baseline” case (>99.9999% purity by metals basis vs. >99.99%). Because 99.9999% pure SnS feedstock is not commercially available, I cannot simply reproduce current growth techniques with higher-purity materials. I will also show in Section 2.7.2 that it is not possible to purify commercial feedstock by simple methods such as evaporative purification. Instead I develop a growth technique for SnS films in which I sulfurize high-purity Sn in H$_2$S gas. I will refer to films grown from 99.99% pure (“4N”) and 99.9999% pure (“6N”) feedstocks as “4N films” and “6N films”, respectively.

I attempt to quantify reduction in contamination levels using a variety of analytical techniques. I then measure carrier transport properties, particularly the minority-carrier lifetime, in 4N and 6N films to test the hypothesis that contamination is limiting SnS material performance. In agreement with the above hypotheses, I demonstrate a significant increase in minority-carrier lifetime for 6N films, which is predicted by device simulations to result in higher efficiencies for SnS PV cells.
Chapter 2
Theory

This study encompasses several aspects of materials development and modelling. SnS films are fabricated and analyzed for their defect makeup and material quality. This section will cover the theory and history behind carrier transport in semiconductors; crystal growth, particularly of SnS; and intrinsic and extrinsic defect formation under varying chemical and physical environments.

2.1 Charge transport in solar cells

Good semiconductor charge transport is critical for high-performing photovoltaic devices. I will describe device operation assuming an inorganic p-type material, i.e., a material in which there are, on average, more empty valence band (VB) states than there are full conduction band (CB) states. However this logic can be generalized to n-type material as well (where the reverse is true).

Under device operation, electrons are excited from a VB state to a CB state via photons with energy equal to or greater than the difference between the VB and CB energy levels (known as the bandgap, $E_g$). The empty VB state left behind acts like it has positive charge, and this quasiparticle consisting of the absence of an electron is known as an electron hole (referred to hereafter simply as a hole). Electrons in the sparsely-filled CB are unlikely to encounter other filled CB states and are free to move through the material. A combination of an internal electric field (generated by forming a junction between the p-type material and an n-type material, known as a p-n junction), as well as a diffusion gradient, cause these unbound electrons in the CB to move towards an electrical contact. Holes in the VB, by the same reasoning, move towards the opposite contact. This process is illustrated below. Note that this diagram does not account for advanced aspects of p-n junctions, such as band bending or varying bias conditions. A more thorough treatment of p-n junctions can be found in several PV textbooks [27], [28].
Figure 2.1: Simplified carrier transport in an inorganic solar cell. Electrons are excited from VB to CB by a photon. They leave behind an empty state, which acts as a positive charge carrier and is known as a “hole”. Under an internal electric field \( E \), electrons in the conduction band are free to travel to one end of the material, while holes travel to the other.

However, an electron may not make it all the way to a contact. It may encounter a hole and relax down to occupy this empty state. Holes can be empty states in the valence band, or in a mid-gap electronic state caused by a defect. Upon relaxation, the electron releases energy as photons or phonons in a process known as recombination. Radiative recombination typically refers to relaxation from a CB state to a VB state (or shallow defect states near the bands) and results in emission of a photon with energy approximately equal to the bandgap. This photon can re-excite a neighboring electron. Non-radiative recombination refers to relaxation through a mid-gap defect state. Typically in this case most of the energy is dissipated via momentum transfer to the lattice (i.e., phonon emission) which does not excite nearby electrons. The details and statistics of recombination are explained in Section 2.3.

An excited charge carrier (electron or hole) will persist in the excited state for a characteristic period of time before it recombines. This characteristic time is known as the carrier lifetime \( \tau \) [s]. We are primarily concerned with the lifetime of minority carriers (in a \( p \)-type material, these are electrons). A carrier will also diffuse through a material under an applied gradient depending on a parameter known as carrier mobility, \( \mu [m^2/(Vs)] \).

The average distance a carrier can move through a given material is given by the diffusion length, which is the square root of the product of the electron diffusivity, \( D_{e} \), and the carrier lifetime.

\[
L_D = \sqrt{D_e \tau} \quad (2.1)
\]
The Einstein relation relates the diffusivity of a charged particle at equilibrium with its charge $q$, its mobility, the Boltzmann constant $k$, and the temperature $T$

$$D = \frac{\mu k T}{q} \quad (2.2)$$

Then we can say for carriers with fundamental charge $e$, that

$$L_D = \sqrt{\frac{\mu T k T}{e}} \quad (2.3)$$

In order to extract charge from all points of a semiconductor, the diffusion length should be long enough to allow an excited carrier to reach an electrical contact before recombining (i.e., approximately the thickness of the semiconductor layer).

Carrier mobility in SnS is up to $\sim 40 \text{ cm}^2/(\text{Vs})$ – comparable with some high-performing Cu(InGa)Se$_2$ [29], [30]. However, SnS is limited by low carrier lifetimes of $<100 \text{ ps}$ [24]. Modelling done in our group for SnS shows that increasing the lifetime by 1—2 orders of magnitude will allow for $10+\%$ device efficiency assuming current cell architectures [15], as shown below:

![Figure 2.2: SnS device efficiency vs. hole concentration and minority-carrier lifetime for a given SnS cell architecture. Carrier concentrations in our baseline devices can range over several orders of magnitude, and lifetimes are $<100 \text{ ps}$ (indicated by red circle), limiting device efficiencies to $\sim 4\%$ or less. A 1- to 2-fold increase in lifetime could pave the way for up to 10% efficient devices (figure credit: Niall Mangan).](image)
Increasing minority-carrier lifetime is thus a critical step in achieving better solar cells. The aim of the present study is to increase minority-carrier lifetime by reducing recombination through defects.

2.2 Point defects and terminology

A perfect crystalline lattice is made of a repeating pattern of atoms, such that there is a representative unit cell which can describe the entire ordering of the crystal. Across each tessellation of this repeating unit cell, both the geometric orientation and chemical makeup of each atomic site is identical. This perfect lattice can be disrupted by single-atom imperfections, or imperfections that incorporate lines or planes of atoms. These are referred to as point and extended defects, respectively. This study will only consider point defects, with the knowledge that extended defects may play a large role in SnS as well. I will use the terms defect and point defect interchangeably for the rest of this study unless otherwise specified.

Point defects can be placed into two classifications: intrinsic and extrinsic. Intrinsic point defects refer to atoms of the host lattice (i.e., atoms which make up the repeating unit cell) which have migrated from their equilibrium position, while extrinsic defects involve a foreign (non-host) atom. Each of these defects corresponds to a perturbation in the local chemical environment. As such, electrons interacting with these defects have a different energy than those within the repeating matrix. This has the effect of introducing energy states that differ from the band structure of the crystal.

The most common point defects are vacancies (in which an atom is missing from its typical lattice site), antisites and substitutions (in which an incorrect atom is sitting on another atom’s lattice site), and interstitials (in which an atom is squeezed in between lattice sites).

Kroeger-Vink defect notation is used to describe defects. A vacancy of atom A is denoted $V_A$. The substitution of a B atom on an A lattice site is denoted $B_A$. An A atom occupying an interstitial site is denoted $A_i$. Examples of intrinsic defects in SnS include the Sn vacancy $V_{Sn}$ or interstitial $Sn_i$. Common extrinsic defects may include oxidation products $O_S$ or $O_i$, or sodium substitution on a Sn site $Na_{Sn}$. Examples of intrinsic and extrinsic defects are shown below:
Figure 2.3: Point defects in a repeating lattice of A and B atoms. Intrinsic defects include the vacancy of an A atom ($V_A$), a B atom substituting on an A lattice site ($B_A$), and an A atom occupying an interstitial site ($A_i$). An example of an extrinsic defect is the substitution of an impurity atom, C, on a B site ($C_B$).

Specific terminology is used in this study to describe defects, particularly extrinsic defects. Contaminants, or impurities, are defined as any element that is not of the host matrix. An impurity element can be located anywhere in the material, and may or may not be incorporated into the crystal lattice as a defect. Extrinsic defects are point defects in which at least one of the participant atoms is an impurity. These defects may not be electrically active, but they are incorporated into the crystal lattice and can be ionized given the correct electronic conditions (i.e., Fermi level placement).

For semiconductor devices these defects can range from benign to disastrous depending on the energetics of the defect. If defects lie outside of the bandgap, then these states are either always full (if they lie within the VB) or always empty (in the CB) and are thus electrically benign. Even if they lie within the bandgap but very near the band edges, they may acts as dopants (i.e., modulate the material's free carrier concentration and thus Fermi level) but are not necessarily detrimental in terms of carrier recombination. In fact the ability to manipulate the Fermi level of semiconducting materials (by doping the material p-type or n-type) is a key aspect of forming a p-n junction particularly in silicon solar cells. Intrinsic defects can be used to modulate hole concentration in many PV-relevant absorber materials, for example CuIn$_x$Ga$_{1-x}$Se$_2$ and Cu$_2$ZnSnS$_4$ [13]. Extrinsic levels due to phosphorus or boron incorporation are used to dope Si n-type or p-type, respectively [31].

However, it is possible for these defect energy states to lie relatively deep within the bandgap, and act as non-radiative recombination centers. This has the effect that any electron above the defect level (i.e., an electron in the conduction band) is energetically driven to
recombine via an empty defect state without emitting a useful photon. The effect is exacerbated as defect states approach the middle of the bandgap. Iron, for instance, is known to form interstitial defects (Fe$_i$) with mid-gap energy levels in crystalline silicon. Combined with the fact that Fe$_i$ in silicon is able to affect electrons within a large area – known as the capture cross section – even small amounts can have dire ramifications on recombination rates within the material, and thus the material’s minority-carrier lifetime [32]–[34].

Significant work has been done to understand intrinsic and extrinsic defects in a variety of semiconducting compounds, and several well-established theories exist to model defect formation and defect-mediated recombination in semiconductor materials. Two in particular will be discussed in detail below. Shockley-Read-Hall statistics quantify the rate of electron transfer between band states and defect states, and can be used to predict carrier lifetimes. Kroeger-Vink defect chemistry theory treats defect formation using the laws of mass action, in which defect concentrations are products of an Arrhenius relationship that uses a characteristic formation enthalpy for each defect type.

2.3 Shockley-Read-Hall recombination statistics

It is critical to understand electron transfer between electronic states in a semiconductor in order to minimize the recombination current. Shockley-Read-Hall (SRH) statistics describe these transitions [35]. For simplicity, all phenomena will be described for electrons in a $p$-type material. However, the same logic generalizes to holes in an $n$-type material.

Electronic states of interest can consist of valence and conduction band states, as well as electronic states within the bandgap caused by point defects. An electron can be excited from the valence to the conduction band, or to a defect level – e.g. by a photon of energy greater than or equal to the difference in energy between these states. For VB→CB transitions, this energy is typically equal to $E_g$.

This electron can then decay from this excited state to a lower-energy state by recombining with a hole via either radiative or non-radiative recombination (i.e., if the hole is in the valence band or in a defect state, respectively).

If the electron fills an empty defect state, it can further recombine with a hole in the valence band, or be re-excited back into the conduction band. This process does not release phonons – energy is primarily dissipated by phonon emission instead which does not excite neighboring electrons. Non-radiative recombination is a large potential loss mechanism in devices and is significantly less desirable than radiative recombination.

When describing the statistics of defect-mediated recombination, it is common to refer to all movement of carriers from a band state to a defect state as “capture”, while movement from a defect state to a band state is termed “emission”. These processes and naming conventions are illustrated below, assuming sharp band edges:
A material which is dominated by radiative recombination, *i.e.*, only processes *a* and *b*, is considered to be intrinsic. Some real materials do act as intrinsic, particularly high-purity materials under high illumination conditions in which excited electrons vastly outnumber trap states and thus fill all traps. For this study, however, it is assumed that our SnS thin films are limited by extrinsic contamination. Thus the focus of this study will be the application of SRH statistics to defect-mediated recombination.

Let us first consider electron capture – process *e* – in the simple case of an electron injected into the CB of a highly *p*-type material. We assume all defects are occupied by holes, and any electron which “finds” a defect will instantly be captured and recombine. The capture rate for electrons $C_n$ [s$^{-1}$] in this simple case is the product of the thermal electron velocity $v$ [m/s], the density of traps $N_t$ [m$^{-3}$], and the capture cross section $\sigma$ [m$^2$], which is defined as the 2-D area for which any carrier that passes through will be drawn into the defect state and trapped. We then define a characteristic lifetime for electrons in a highly *p*-type material as the inverse of this capture rate:

$$\tau_{0,n} = \frac{1}{C_n} = \frac{1}{v \sigma n N_t}$$  \hspace{1cm} (2.4)

We will assume for simplicity that it is sufficient to average $C$ across the entire conduction band (or valence band for the case of holes) in nondegenerate materials, and thus $C$ is an energy-independent scalar for a particular defect.

We can similarly define the lifetime for holes in a strongly *n*-type sample as $\tau_{0,p}$. Depending on the material, these may not be the same, as capture cross sections for a given
defect may change drastically for holes vs. electrons in the same material (particularly if the
defect is charged).

The assumption of highly doped materials is rarely valid, however. In many cases a
fraction of defects as well as bands are filled. We can use Fermi-Dirac statistics to predict the
probability that a given state (either defect state or band state) will be filled with an electron as:

$$f_n(E) = \frac{1}{1 + e^{(E - E_{F,n})/kT}} \quad (2.5)$$

where \( E \) is the energy of the state and \( E_{F,n} \) is the quasi-Fermi energy for electrons. The
analogous probability for holes is simply \( f_p = 1 - f_n \).

The capture rate \( R_n \) for an electron moving from a conduction band state with energy
between \( E + dE \) to a defect state of energy \( E_t \) is a product of the capture rate for an electron
injected into a p-type material (\( C_n \), above), multiplied by the density of electrons available in the
conduction band (which is simply the band density of states \( N(E) \) multiplied by the probability
that a band state is occupied by an electron, \( f_n(E) \)), and multiplied by the probability that the trap
state is occupied by a hole, \( f_{t,p} \).

$$R_n = C_n f_{t,p}(E) N_c(E) f_n(E) \, dE \quad (2.6)$$

We can create a similar expression for electron emission from a defect state, as well as
hole capture and emission. By balancing these at equilibrium conditions and assuming
nondegenerate material, we can derive the net capture rate as

$$U_{c,n} = \left( 1 - e^{-E_t/E_{F,n}} \right) f_{t,p} n C_n \quad (2.7)$$

where \( n \) is the number of electrons in the conduction band and can be related to \( N_c \) and
\( E_{F,n} \), as well as the lowest conduction band energy \( E_C \):

$$n = N_c e^{(E_{F,n} - E_C)/kT} \quad (2.8)$$

We then define the density of occupied trap states as

$$n_1 = N_c e^{(E_t - E_C)/kT} \quad (2.9)$$

and, if we assume a near-empty conduction band, \( U_{c,n} \) simplifies to

$$U_{c,n} = C_n f_{t,p} n - C_n f_t n_1 \quad (2.10)$$

with a similar expression for the net hole capture rate \( U_{c,p} \). Setting electron and hole
capture rates as equal under steady-state conditions, in which a constant excitation is equal to a
constant recombination rate \( U \), we get:

$$U = \frac{C_n C_p (p n - p_1 n_1)}{C_n (n + n_1) + C_p (p + p_1)} \quad (2.11)$$

We can state that under a steady carrier generation / recombination rate \( U \), \( n = n_0 + dn \). In
other words electrons in the conduction band are equal to their thermal equilibrium values \( n_0 \).
plus some perturbation due to the excitation \(dn\). Similarly, \(p = p_0 + dp = p_0 + dn\), since all excited electrons result in an equal number of holes.

We can define the electron lifetime in this material as the ratio of this perturbation \(dn\) to the generation rate \(U\):

\[
\tau \equiv \frac{dn}{U}\quad (2.12)
\]

And using the definition \(\tau_0 \equiv \frac{1}{c}\) we finally derive that

\[
\tau = \tau_{0,p} \frac{(n_0+n_1+dn)}{(n_0+p_0+dn)} + \tau_{0,n} \frac{(p_0+p_1+dn)}{(n_0+p_0+dn)}\quad (2.13)
\]

This derivation is for a material with a single defect. However if many defects are present, they act as parallel current pathways. Recombination currents add, and because of the inverse relationship between recombination rate \(U\) and lifetime, the total bulk lifetime for the material is the harmonic sum of the lifetimes of each individual recombination pathway. Note that each defect has its own unique set of parameters including capture cross section and mid-gap energy.

\[
\frac{1}{\tau_{eff}} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \ldots
\quad (2.14)
\]

The effective lifetime should also take into account the intrinsic material lifetime and non-SRH lifetimes such as surface recombination – these can be added into the harmonic sum. More rigorous treatments of this derivation can be found in the literature [35], [36].

We can see that several factors are critical to maintain a high effective lifetime. At first pass, we see that we desire as few non-radiative recombination pathways as possible, and thus as few defects as possible. However, not all defects are equal in severity.

Due to the exponential relationships for \(n_1\) and \(p_1\), \(\tau\) is minimized when \(E_C - E_i = E_i - E_v\). This indicates that the recombination rate for carriers through a given defect is most severe for defects that lie directly in the middle of the bandgap.

Moreover, \(\tau\) is highly dependent on \(\tau_{0,p}\) and \(\tau_{0,n}\) which are inversely proportional to capture cross section \(\sigma\). High values of \(\sigma\) can result in high recombination current even at low defect concentrations. The magnitude of \(\sigma\) is affected by the material’s dielectric constant (higher permittivity suppresses capture cross section), as well as the charge state of the defect (positively charged defects have a higher \(\sigma_n\) and a lower \(\sigma_p\), and vice versa for negatively charge defects).
2.4 Crystal growth

2.4.1 – SnS crystal growth at equilibrium

SnS crystal growth can be understood in the context of the tin-sulfur equilibrium phase diagram, which has been studied in depth and is reproduced below [37].

![Phase diagram of the Sn-S system. α-SnS forms in a thin parameter space when Sn and S are stoichiometrically equal, and at temperatures below the phase transition at ~602°C. Reproduced from Sharma et al., 1986 [37].](image)

When SnS is grown under equilibrium conditions from Sn and S, pure-phase α-SnS (hereafter referred to simply as SnS) forms in a thin line of the parameter space where Sn and S are stoichiometrically equal, and the temperature is below 602°C. This material has space group Pnma, and the crystal structure illustrated below:
Figure 2.6: Crystal structure of α-SnS. The material forms stacked thin sheets similar to graphite. The crystallographic axis convention used in this study is shown as well, with the (100) plane aligned parallel to the stacked sheets. Distances written on the axes are the dimensions of the orthorhombic unit cell.

The Sn-rich side of the Sn-S system (below 602°C) forms a mixture of Sn and SnS. This is unfavorable from the point of view of optimizing intrinsic defects – it is expected that mid-gap defect density is reduced under S-rich conditions [25], [26], [38]. Optimizing point defect concentrations in SnS is discussed below in Section 2.5. Moreover, in a photovoltaic device Sn may act as a high-conductivity electrical pathway through the device, thus creating shunts and reducing $V_{OC}$. The S-rich side of this line, while potentially optimal in terms of intrinsic defect chemistry, runs the risk of forming sulfur-rich Sn$_2$S$_3$ or even the highly sulfurized SnS$_2$ phases. These materials have their own band structures and properties, which may form carrier-blocking or otherwise deleterious junctions with SnS [39]. Thus, phase purity is critical for device performance.

From the point of view of this study, it is particularly important to avoid sulfur-rich phases. The carrier lifetime measurements performed for this study, which are performed via luminescence techniques, may be sensitive to Sn$_2$S$_3$ and SnS$_2$ phases. Any junctions between these and SnS may result in band bending in the SnS, giving inaccurate data. The secondary phases may even themselves luminesce by band-to-band or defect-mediated recombination. The presence of metallic Sn, while less likely to result in a false luminescence signal, could introduce shunt pathways in devices.
To expand the phase diagram to SnS grown under an H₂S atmosphere, I used the thermodynamic modelling program FactSage [40] to compute the lowest-energy state at a given temperature and H₂S pressure, assuming a total pressure of 0.5 atm as this closely approximates the experimental conditions under which I sulfurize Sn.

![Phase diagram of the Sn-H₂S system](image)

**Figure 2.7:** Phase diagram of the Sn-H₂S system, with a constant total pressure of 0.5 atm. α-SnS is desired for this study, and is formed in a large region below 600°C for a large range of H₂S pressures. The maximum achievable H₂S pressure for this study is ~0.02 atm, ensuring pure-phase SnS if the system is allowed to reach equilibrium. Note that "gas" indicates a mixture of primarily H₂, H₂S, and SnS.

This equilibrium phase diagram indicates that for all temperatures achievable in my experimental setup (25-600°C), and achievable H₂S partial pressures (>~0.02 atm), I should form the desired α-SnS. However, as will be discussed in Section 2.4.2 below, the kinetics of this reaction may be slow because of the energetic barrier to dissociating H₂S molecules. Thus, in order to sulfurize Sn films into SnS relatively quickly, higher temperatures are required.

A balance must be struck, however. During growth I use a gas flow furnace, in which reactive H₂S gas is flowed very slowly over Sn films (this is discussed further in Section 3.5). Thus, this is not an equilibrium process. Moreover, there exists a small amount of SnS(g) above solid SnS. This gas will be swept away by the flow within the furnace, removing material from
the thin film. As temperatures rise, the SnS vapor pressure rises, and it has been observed that if temperatures are too high the film will evaporate entirely.

That said, the equilibrium phase diagram can still guide SnS growth. Past work has shown the success of growing SnS single crystals under equilibrium conditions by sulfurization in H₂S or elemental S. One of the simpler methods is melting Sn and S under an H₂S / H₂ atmosphere in a closed environment and allowing the system to cool slowly [25]. More complex methods have been tried, ranging from chemical vapor transport using iodine [39]; to zone melt growth [41]; to Bridgman-Stockbarger refinement of polycrystalline SnS [42]. While these methods vary greatly, the goal is the same: raise a near-stoichiometric mixture of Sn and S and/or H₂S above the melting point (880°C) and allow the material to cool slowly and solidify at near-equilibrium in its lowest-energy state, in which there are few or no grain boundaries.

2.4.2 – Crystal growth kinetics: thin film growth

Controlling the growth of SnS crystalline thin films is critical for this study as well as for producing high-efficiency devices. This study focuses primarily on the achievement of pure-phase SnS via sulfurization of Sn in a sulfurous atmosphere. The development of thin films over time as a function of process parameters can be understood via the kinetics of grain formation. A deeper treatment of this theory can be found in materials science textbooks [43].

Crystals form by nucleation of atoms into solid crystalline clusters, which grow into full crystals. We will consider the case of anisotropic, spherical crystals composed of element A forming from a gas of monoatomic A atoms. The driving force for nucleation of a crystal derives from a competition between the energy benefit of forming crystalline A-A bonds, and the energy penalty due to the creation of extra surface area, and thus extra dangling surface bonds. The free energy change for cluster formation as a function of cluster radius \( r \) is then:

\[
\Delta g = 4\pi r^2 \gamma_s + \frac{4}{3} \pi r^3 \Delta g^{\text{v} \rightarrow \text{s}}
\]

where \( \gamma_s \) is the energy per unit surface area of a new nucleus (which in real systems will be substrate / matrix dependent), and \( \Delta g^{\text{v} \rightarrow \text{s}} \) is the total free energy change due to creation of crystal bonds. This must be negative for any nucleation to occur.

As clusters grow, there is a critical radius \( r^* \) where the volumetric energy benefit outweighs the surface area energy penalty and \( \Delta g \) becomes negative. The nucleation rate is defined as the rate at which clusters of adsorbed A atoms exceed this critical radius, which is taken as the radius at which the free energy change reaches a local maximum. We calculate this critical radius by setting:

\[
\frac{d\Delta g}{dr} = 0 = 8\pi r^* \gamma_s + 4\pi r^{*2} \Delta g^{\text{v} \rightarrow \text{s}}
\]
The free energy barrier at this radius can be found by plugging the value of $r^*$ into the formula for $\Delta g$:

$$r^* = -\frac{2\gamma_s}{\Delta g^*_A}$$  \hspace{1cm} (2.17)

The free energy barrier at this radius can be found by plugging the value of $r^*$ into the formula for $\Delta g$:

$$\Delta g^* = \frac{16\pi\gamma_s^3}{3(\Delta g^*_A)^3}$$  \hspace{1cm} (2.18)

Now that we know the driving energy for nucleation and the associated activation barrier, we can define the nucleation rate as the product of the rate at which gas atoms strike a given area, the surface area of a critical cluster, the number of critical clusters in the system, and an Arrhenius term which describes the probability that a gas atom will adhere to a critical cluster (the free energy change for this interaction, as described above, is $\Delta g^*$).

$$\dot{N} = \frac{P}{\sqrt{2\pi mkT}}(4\pi r^*{}^2)N_{tot}e^{-\frac{\Delta g^*}{kT}}$$  \hspace{1cm} (2.19)

Figure 2.8: Free energy change for a nucleating spherical particle as a function of radius. A critical radius exists at which the volumetric free energy benefit outweighs the surface energy penalty, after which nucleation is favorable. Nucleation rate is defined as the rate at which particles which exceed this critical radius.

Now that we know the driving energy for nucleation and the associated activation barrier, we can define the nucleation rate as the product of the rate at which gas atoms strike a given area, the surface area of a critical cluster, the number of critical clusters in the system, and an Arrhenius term which describes the probability that a gas atom will adhere to a critical cluster (the free energy change for this interaction, as described above, is $\Delta g^*$).

To apply this theory to SnS nucleating in a solid Sn film with H$_2$S gas, we can approximate $\Delta g^{v\rightarrow g}$ as the free energy difference due to destruction of one H$_2$S molecule and creation an S-Sn bond, which can be looked up in thermodynamic tables as $\Delta g^{v\rightarrow g} = 7.46 - 4.90 \approx 2.56$ eV/molecule at room temperature [44], [45]. At first approximation it would seem that
very high temperatures are required to drive this reaction \( (kT = 14.26 \text{ eV at nearly } 30,000 \text{ K}). \) However, the catalysis of H\(_2\)S on various transition metals and metal sulfides has shown significant decomposition at several hundred degrees celcius [46], [47] (although to my knowledge this reaction has not been studied extensively on tin).

So, this simple model of growth kinetics can only serve as a guide for SnS growth via sulfurization of Sn films with H\(_2\)S without further study of surface kinetics in H\(_2\)S gas, as well as knowing certain of the material constants above. However, similar trends should apply – to achieve full sulfurization of Sn films (as long as I am not concerned with nucleation density), I required high H\(_2\)S pressure, and temperature that is high enough to allow the sulfur bonds to reform, but not so high as to convert the material to \( \beta \)-SnS or evaporate it entirely (see section 2.4.1 above regarding the SnS phase diagram). To increase grain size, by contrast, I would want to grow at a lower temperature and H\(_2\)S pressure for long times.

SnS thin films have been grown via a variety of methods. Some of these are beholden to the SnS phase diagram: sulfurizing Sn films, either by evaporating elemental sulfur in a closed environment [48], [49], or flowing H\(_2\)S over the films [50], as well as chemical bath deposition [51].

Others sidestep these thermodynamics. Thermal evaporation (TE) has achieved near-record SnS efficiencies and takes advantage of the fact that at low temperatures SnS evaporates congruently and thus is able to self-regulate its stoichiometry [23]. Sputtering of SnS targets [52] or pulsed laser deposition [53] have also demonstrated stoichiometric, phase-pure films.

Thermal evaporation is used as the “baseline” deposition method in this study for SnS thin films. The effects of annealing SnS under a variety of conditions, both on morphology as well as optoelectronic properties, are investigated in the thesis of former lab member Dr. Katy Hartman [54]. Morphology as observed by SEM micrographs is shown below for SnS thin films deposited by thermal evaporation, and then subjected to several different annealing conditions. While the grain size changes between samples, it is clear that a distinct morphological shift occurs after even short annealing times (5-10 minutes).
2.5 Intrinsic defects

2.5.1 Kroeger-Vink defect chemistry theory

Once a crystalline material is grown, it is often important to understand what defects are present within the material. These defects, whether intrinsic or extrinsic, form naturally during growth and processing. The relative concentrations of defects can be predicted by the use of Kroeger-Vink defect chemistry theory (referred to hereafter as K-V theory).

K-V theory solves a system of equilibrium equations for defect formation. The number and form of these equations depends on how many and which defects we choose to treat by this model. Thus, this model readily breaks down if other unknown defects are prevalent in a material. The addition of another formation equation could significantly change the predicted defect concentrations. It will be shown below that the SnS samples used for this study do not conform to a simple K-V model. This is likely caused by a more complex defect profile with a combination of intrinsic and extrinsic defects.
K-V theory uses kinetic theory of mass action to predict defect concentrations in a crystalline lattice [55]. Consider a lattice of a crystal phase α constituting only A atoms. The α crystal is in contact with a gas composed of monoatomic A. In the simplest case, we will assume the only possible defect is the absence of an A atom from a lattice site (i.e., an A vacancy, VA). For this simple case we will ignore the possibility of interstitials or extrinsic defects.

A vacancy of A (usually) causes an increase in the system energy, due to the dangling bonds that result at the vacant site. The formation enthalpy for the vacancy, $E_{f,V}$, is defined as the difference in energy between a perfect crystal with and without one single vacancy. We also can say that desorption (or adsorption) of an A atom between the crystal and gas phase causes a change in enthalpy equal to the bonding enthalpy of an A atom at the crystal/gas interface, denoted $E_a$.

With no other defects present, we can then use Arrhenius relationships to define reaction constants, $K$, for two basic reactions: 1) in which a surface atom $A_{\text{surf}}$ desorbs from the $\alpha$ lattice and becomes gaseous, and 2) in which a bulk A atom migrates to the surface to fill the space of the desorbed atom, leaving behind a vacancy.

$$A_{\text{surf}} \leftrightarrow A_{\text{gas}} \quad K_d = \frac{P_A}{[A_{\text{surf}}]} = K_{d,0}e^{-E_d/kT} \quad (2.20)$$

$$\text{Null} \leftrightarrow V_A + A_{\text{surf}} \quad K_v = [V_A][A_{\text{surf}}] = K_{v,0}e^{-E_{f,V}/kT} \quad (2.21)$$

where $P_A$ denotes the pressure of gas A, null denotes a defect-free crystal, and $K_{v,0}$ and $K_{d,0}$ are temperature-independent constants which take into account the entropy change for each reaction.

We can then consider the likelihood that a given defect state will become charged by absorbing either a positive or negative charge carrier. Let us assume that the A vacancy is a $p$-type dopant with an energy level equal to $E_V$ above the valence band maximum ($E_{VBM} + E_v$). We define the Fermi level as having an energy equal to $E_F$ above the valence band maximum. The corresponding reaction and reaction constant are:

$$V_A \leftrightarrow V_A^- + h^+ \quad K_p = \frac{[p][V_A^-]}{[V_A]} = K_{p,0}e^{(E_F-E_V)/kT} \quad (2.22)$$

where $[p] = [h^+]$ denotes the concentration of free holes, or positive charge carriers. The statistics of defect state occupation are given in Section 2.3.

We must also consider the reaction in which a valence band electron spontaneously excites through the bandgap of energy $E_g$ to the conduction band, generating an excited free electron in the conduction band and leaving behind a free hole in the valence band:

$$\text{Null} \leftrightarrow e^- + h^+ \quad K_i = [n][p] = K_{i,0}e^{-E_g/kT} \quad (2.23)$$

Lastly, we may assume that the crystal as a whole is not charged, and so positive and negative charges must balance:

$$[p] = [n] + V_A^- \quad (2.24)$$
These equations constrain the system sufficiently to solve for hole concentration as a function of temperature and the partial pressure of A atoms above the α phase:

\[ K_i = [p]([p] - [V_A^-]) = [p] \left( [p] - \frac{K_i' [V_A]}{[p]} \right) = [p] \left( [p] - \frac{K_i' K_V K_d}{[p] P_A} \right) \] (2.25)

\[ [p] = \sqrt{K_i + \frac{K_i' K_V K_d}{P_A}} \] (2.26)

where all the reaction constants \( K \) are functions of the entropy and enthalpy changes for the corresponding chemical reaction, as well as the ambient temperature.

This theory can be generalized to more complex cases, in which the lattice consists of multiple elements and the gas phase is not necessarily monoatomic. Particularly, this theory has been applied to SnS to determine the dependence of \([p]\) on ambient \( S_2 \) gas pressure [25, 26].

Assuming that the Sn vacancies only occupy the doubly-ionized state \( V_{Sn}^{2-} \), and that under sulfur-rich conditions the \( V_{Sn} \) defect concentration is much greater than all other defects, we can solve for:

\[ [p] = 2 [V_{Sn}^{2-}] = 2 \left[ K_d e^{-\left( \frac{E_{V_{Sn}^{2-}}}{kT} \right)} P_{S_2}^{1/2} \right]^{1/3} \] (2.27)

where \( E_{V_{Sn}^{2-}} \) denotes the formation enthalpy for a charged Sn vacancy, and \( K_{ads} \) is here the reaction constant for adsorption of a sulfur atom onto the surface of an SnS lattice. We can see that hole concentration should scale with the 6th root of the sulfur partial pressure, and thus the log of \([p]\) should rise vs. the log of \( P_{S_2} \) with a slope of 1/6. It should also increase with temperature according to the Arrhenius relationships for adsorption of an S atom onto the lattice surface, as well as for the formation of a charged vacancy.

In these studies, SnS was annealed under a variety of pressure and temperature conditions for long times (until the system reached equilibrium). The experimental carrier concentrations are compared to those predicted by K-V theory and shown below. In both the temperature and pressure case, there is quite good agreement between model and experiment. This suggests that in these crystals, hole concentration is indeed controlled only by the doubly-charged Sn vacancy \( V_{Sn}^{2-} \). Moreover, these results agree with the predicted slope of 1/6 of \( \log([p]) \) vs. \( \log(P_{S_2}) \).
Figure 2.10: Carrier concentration in SnS vs. processing conditions – a) partial pressure of sulfur gas and b) temperature during annealing. Lines are predicted from K-V theory, while points are measured experimentally. Figures a and b from Rau, 1966 [25] and Albers et al., 1961 [26], respectively.

During the thesis work of former lab member Dr. Katy Hartman, to which I contributed, she attempted to reproduce the effects on carrier concentration in SnS single-crystals reported in these papers, but now measuring on PV-relevant SnS thin films as well as single crystals grown by iodine-assisted vapor transport [54]. It should be noted that Dr. Hartman performed all sample preparation and data analysis for thin film samples, while I performed these tasks for single-crystal samples. All experimental runs were performed by both of us in tandem.

Thin films were identically pre-processed to induce grain growth before these experiments, in order to rule out effects of film densification. Different large-grained film and crystal samples were then subjected to different annealing profiles (both temperature and pressure) and the resulting carrier concentration for each sample was plotted against the annealing conditions. Based on the literature, we expected to see an increase in carrier concentration with both temperature and sulfur partial pressure, and that the log of the carrier concentration should increase as 1/6\(^{th}\) the log of the sulfur pressure. Observed carrier concentrations before and after annealing as a function of annealing temperature and pressure are shown below:
Figure 2.11: Carrier concentrations in SnS single crystals and SnS large-grained thin films after annealing. Resulting carrier concentration is plotted as a function of a) Annealing temperature and b) $S_2$ partial pressure while annealing. Slight or no change in carrier concentration is seen in either sample set regardless of anneal conditions – rather, most annealed samples fall in or near the baseline range for un-annealed samples.

A surprising effect was seen: although the carrier concentration increased during pre-processing of thin films, further anneals of films and crystals were not able to significantly change the carrier concentration in these samples. Two primary hypotheses were conceived:
1) The dense morphology of large-grained films and single crystals kinetically limit point defect diffusion (this would not be true for the initial pre-processing, when films still show high surface-area-to-volume, which could account for the initial change to hole concentration. Or,

2) Extrinsic contamination such as sodium diffuses into the material at the elevated annealing temperatures and acts as a p-type dopant, obscuring any changes to intrinsic defect concentration.

Both hypotheses are investigated in the course of this study. It is shown that densification does not seem to affect changes to carrier concentration, but rather any anneal at all caused the carrier concentration in SnS to reach approximately the same value. It was deduced that extrinsic, rather than intrinsic, defects, may be dominating SnS — in this case, sodium indiffusion could be masking any changes to the intrinsic defect profile. The rest of the study, which deals with extrinsic contamination, is motivated by this finding.

2.5.2 Advanced modelling

More comprehensive computational techniques have been used to evaluate the properties of intrinsic defects in thin film semiconductors. Density functional theory (DFT) calculates a material’s electronic structure from first principles. This technique has been used to calculate SnS band structure [38], [39], [56], as well as the formation energies and energetic position within the bandgap for various defects [38], [56] Calculated mid-gap states and formation energies for intrinsic point defects in SnS are shown below.
Figure 2.12: Mid-gap levels and formation energies for intrinsic defects in SnS, calculated via DFT for the S-rich and Sn-rich ends of the SnS phase diagram. Formation enthalpy for each defect is related to its solubility in the crystal. The location of inflection points along the x-axis indicate energetic levels within the bandgap. Under S-rich growth conditions, the Sn vacancy is predicted to dominate in its doubly-ionized form $V_{Sn^{2+}}$. Reproduced from Malone et al. [38].

These plots show formation enthalpy ($\Delta H_f$) of a given defect as a function of the Fermi level ($E_F$) between the valence band maximum (on the left) and conduction band minimum (on the right). The formation enthalpy represents the difference in system energy between a perfect lattice, and a lattice with a single defect introduced into it.

As the average electron energy (i.e., Fermi level, on the x axis) changes, it affects the solubility (formation enthalpy) of charged defects – defects adopt negative or positive charge more easily in n-type or p-type environments, respectively. The observed slope of $H_f$ vs. $E_F$ is directly related to the preferred charge of the defect at that Fermi level (i.e., a slope of +2 indicates a +2 charge, a slope of -1 indicates a -1 charge, etc.).

Changes in slope refer to Fermi energies at which the defect changes charge states. If we imagine the Fermi energy rising, this change corresponds to an electron filling an electronic state introduced by the defect. Thus, the x-axis value of these points indicates the location of defect energy states within the bandgap.

It should be noted that other groups have attempted to model intrinsic defect properties in SnS via DFT. While qualitatively similar, there is some quantitative disagreement between calculated defect energies [56]. This speaks to the limitations of DFT for calculating absolute energy values. Modifications to DFT, such as hybridization with Hartree-Fock functionals [57] are expected to give more quantitative results.
2.7 *Extrinsic defects*

Extrinsic defects can be introduced into a material by a variety of mechanisms. These defects can be due to impurity atoms present in the material feedstock, which are transferred to the semiconductor film during deposition. Contamination can also arise from processing and handling, such as by contact with metal sample holders, biological tissue, or even from human breath or skin particulates.

2.7.1 *Prior work in silicon and other materials*

By comparison to intrinsic defects, little work has been done to assess the impact of impurities for thin film materials, with the notable exceptions of Na in Cu(In,Ga)Se₂ [58]–[60] and Cu₂ZnSnS₄ [61] and Cl in CdTe [62], which have been studied extensively. However, we can borrow knowledge gained from the silicon PV community which has decades’ worth of experience dealing with impurities.

It should be noted that much of this contamination research done for silicon photovoltaics will not be covered in this report. In particular, the groundbreaking work indicating that impurities in silicon decorate structural or extended defects [32], [33], [63], [64] is not addressed in this study. Nor will I address the convolved effects of structural defect and point defect densities on carrier lifetime, which have been well laid-out for silicon [65]. While this topic cannot be addressed in this thesis, structural inhomogeneities may be quite important in thin film materials, which often have higher grain boundary density than silicon. Ongoing and future work in our lab will attempt to provide a more comprehensive view of the role of both point and structural defects in our thin film materials.

Much of the progress in impurity characterization and engineering in silicon occurred by intentionally contaminating extremely high-purity material. By measuring the minority-carrier lifetime of high-purity silicon wafers with precisely controlled quantities of a single contaminant, it is possible to plot performance (either minority-carrier lifetime or efficiency) vs. impurity concentration and deduce the impact of a given contaminant [66]–[68].

As shown in Figure 2.13 below, silicon PV device efficiency falls off above critical concentrations of a given metal contaminant [68]. Similar studies have also demonstrated the deleterious effect of non-metal contaminants such as oxygen [69].
Figure 2.13: Si PV device efficiency vs. impurity concentrations. For every metal, there exists a threshold concentration after which cell efficiency is hampered by the metal impurity. Values given are for 4 Ω-cm $p$-type single-crystalline silicon. Reproduced from Davis et al., 1980 [68].

As explained in detail in Sections 2.2 and 2.3, the impact of a defect on material quality is governed by several characteristic parameters of the defect, in particular: capture cross-section, solid solubility of the defect in the host crystal (defined by a defect formation enthalpy), and energetic level of the defect within the bandgap.

SRH modelling, in particular, can shed light on the effects of a defect. Combined with the intentional contamination studies described above, this sort of modelling can have potent predictive power, and curves similar to the experimental ones shown in Figure 2.13, above, have been reproduced via SRH modelling of impurities in silicon [70], [71]. Such simulations help confirm that the catastrophic efficiency decreases with contamination are due to a corresponding drop-off in carrier lifetime, as shown below:
Figure 2.14: Calculated minority-carrier lifetimes for extrinsic defects in Si under constant injection level. Reduction in lifetime with increasing defect concentration is believed to cause the catastrophic efficiency decreases with high impurity concentrations seen above. Reproduced from the thesis of Dr. Doug Powell [71].

![Graph showing calculated minority-carrier lifetimes for extrinsic defects in Si under constant injection level.](image)

Some first attempts have been made to replicate this type of experiment in the thin films community. Recent work used combinatorial deposition to grow Cu$_2$ZnSn(S,Se)$_4$ with a range of contaminant levels. This study identified iron as having a particularly deleterious effect on device performance beginning at several hundred ppm [72]. Copper diffusing from a metal substrate into GaAs cells over time under relatively modest operating temperatures has similarly been shown to reduce $V_{OC}$, likely by addition of non-radiative recombination centers [73].

### 2.7.2 Modelling in SnS

In order to quantify and model extrinsic defect effects in SnS and other thin films similar to what has been done for silicon, further knowledge of the physical properties of these defects is necessary. To this end, extrinsic defects for SnS have been studied by DFT simulations [38]. Select data is reproduced below for S-rich and Sn-rich conditions for several impurity elements of interest (specifically Na, Cl, Sb, Zn, and O). Sb and Zn (as well as other metal impurities) are present in the SnS and Sn feedstocks used for this study according to vendor feedstock analysis, which are detailed in Section 3.

Other contaminants could be introduced during processing. Na and Cl are present as salt on biological tissue and could potentially contaminate samples if not processed in a cleanroom environment. Samples are exposed to air frequently and some oxygen contamination is...
inevitable. For a more complete analysis of predicted properties for extrinsic defects in SnS refer to Malone et al, 2014 [38].

Figure 2.15: Mid-gap levels and formation energies for extrinsic defects in SnS, calculated via DFT for the S-rich and Sn-rich ends of the SnS phase diagram. Impurities considered are a) Mo and Na, b) Cl and O, c) As and Sb, and d) Zn and Cd. Figure reproduced from Malone et al, 2014 [38].

Of particular note is the extremely low formation enthalpy of the Na\textsubscript{Sn} antisite defect – near-zero or even negative for p-type SnS (i.e., with Fermi energies around 200 meV). While the shallow Na\textsubscript{Sn} acceptor level is unlikely to be a major recombination center (as explained in Section 2.3), this indicates that sodium could positively dope SnS readily, and likely even modest amounts of sodium could contribute significantly to the hole concentration.

In fact, ongoing work in our group has shown that the carrier concentration in SnS is strongly sensitive to adding NaCl during growth and processing.

Other contaminants, such as Sb, As, Mo, or O, are predicted to introduce mid-gap recombination centers. Moreover many metals, including Fe, have not been investigated by DFT in the literature and could potentially be detrimental.
We can also estimate which of the metals present in the feedstock will transfer to the final films. We deposit tin sulfide by thermal evaporation in which SnS feedstock is heated to 550-600°C. Thermodynamic modelling performed for this study via the program FactSage shows that many metal impurities will evaporate with SnS, and thus persist in the final deposited films, as shown below. Note that while NaCl is not present in SnS feedstock initially, it could be transferred during handling of either the feedstock or final films, as described above.

![Figure 2.16](image-url)

**Figure 2.16:** Fraction of metal species in vapor phase with varying temperature. Temperatures considered represent the range to which SnS is exposed through the course of this study. Many compounds found in SnS feedstock are likely to volatilize and thus be incorporated in the deposited film. Cu, Fe, Mo, Ca, Ce, and Co may also be present in feedstock but do not volatilize, and thus may be purified out during deposition.

It should be noted that several contaminants found in SnS feedstock, including Cu, Fe, Mo, Ca, Ce, and Co, do not volatilize within the temperature range of interest, and so these may be purified out during deposition.

Samples further encounter many potential contaminants during processing. During the baseline process, samples come into contact with Inconel (an alloy of Ni-Cr-Fe and containing over a dozen metals) sample holders at ~240°C, and are surrounded by a 4.5N pure quartz tube during annealing at 400+°C.

During the process for fabricating “clean” SnS described in this work, the samples are exposed to the same quartz tube as above, at temperatures up to 550°C. Samples also are placed (mounted on a freshly-cleaned glass sample holder) in a shared-use thermal evaporator. Steps are
taken to prevent contamination from the evaporator chamber walls from reaching the sample. These steps are described in Section 3.4.1.

Armed with the knowledge of feedstock purity, likely contamination pathways during processing, and defect formation energies and mid-gap states, we can begin to identify the most likely lifetime-killing defects in SnS. Though no definitive statements can be made without knowing defect capture cross sections, the most likely culprits will have a high abundance in the feedstock (or be present in processing), evaporate under the same temperature range as SnS, and have associated defects with relatively low formation energy and near-mid-gap energy levels in SnS. Elements which fit this description include Sb, As, Zn, and possibly Cs.
In this study, I investigate the role of intrinsic and extrinsic defects in SnS. As described in Section 2.5.1, the SnS used for this study does not seem to conform to Kroeger-Vink defect theory. Two hypotheses are explored: that morphological changes in the film alter the observed carrier concentration, or that the material is dominated by extrinsic defects. The latter will be shown to be the most likely explanation.

Under the hypothesis that extrinsic contamination may be affecting carrier transport in SnS, I then assess the effects of reducing impurity content in SnS thin films on film quality, specifically the minority-carrier lifetime. I begin by reducing impurity content in the feedstock materials by two orders of magnitude—from >99.99% by metals purity to >99.9999% by metals purity (referred to as 4N and 6N, respectively). Because SnS is not commercially available at 6N purity (but Sn is), I sulfurize thin films made from 6N pure Sn purchased from Alfa Aesar in high-purity 4% H$_2$S in N$_2$ balance obtained from Airgas and 5.5N purity (i.e., 99.995% pure) sulfur obtained from Alfa Aesar. I compare these 6N films against films that our lab currently uses for photovoltaic device applications, which are made by thermally evaporating commercially available 4N pure tin sulfide powder obtained from Sigma Aldrich. These will be referred to as “4N films” and “6N films”, respectively.

The metallic impurity content of all materials and substrates used in this study (for which this information is available) is tabulated below. All units are in ppb. Dashed lines indicate concentrations below detection limits. Sn and S are not included since these constitute the film bulk, while Ar, H, N, and O are excluded as samples see air before and after processing. Note that while the 6N Sn shows about 2.5 ppm impurities, nearly 80% of these are due to carbon. Thus, by metals basis the Sn is actually ~6.5N pure. Note that H$_2$S gas should have no metallic impurities to begin with but is held in a metal container. Thermodynamic modelling via the program FactSage indicates that at room temperature, the vapor pressure of metal-containing molecules in this tank should be imperceptible regardless of tank pressure.

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**Total metals** 20,200 548 570 27,060

**Table 3.1:** Impurity concentrations for all materials and substrates used in this study (where available), obtained from vendor certificates of analysis. Total metal content is summed below. 6N Sn is, as expected, approximately 2 orders of magnitude cleaner than the 4N baseline. H$_2$S, in a metal container at room temperature, is predicted to have negligible metal content in gas form.
These two sets of films – 4N and 6N films – are analyzed and compared. The phase composition of these samples is deduced via X-ray diffraction (XRD), and morphology is analyzed via scanning electron microscopy (SEM). The impurity content of the films is analyzed via secondary ion mass spectrometry (SIMS), inductively coupled plasma mass spectrosopy (ICP-MS), and x-ray fluorescence (XRF). Minority-carrier lifetime is measured via time-correlated single photon counting (TCSPC).

All samples are stored in dust-free sample holders, and utmost care is taken to avoid any contamination of the samples, including wearing facemasks and gloves at all times during sample processing and never allowing anything to come in contact with the sample surface, especially before any high-temperature process step.

It should be noted that for the samples analyzed during this study, all 4N films (i.e., the “baseline” samples) were grown on high-purity float-zone Si substrates, whereas 6N films were grown on 4.5N pure quartz (a few were grown on high-purity float-zone Si for comparison). The exception are the 4N samples made for the intrinsic defect study (results in Section 4.1), which were grown on Si/SiOx substrates. Since 4N films were grown on “clean” Si substrates, and the 6N films were grown on “dirty” quartz substrates, we can be confident that higher contamination in the 4N samples is from the dirty feedstock, while reduced contamination in the 6N samples is not simply due to a cleaner substrate. However, further study will fully compare samples on identical substrates.

3.1 Substrate specifications and cleaning

Quartz and silicon substrates are used in this study. Quartz substrates are 4.5N pure, with primarily Al, Li, and K contamination, and obtained from Quartz Scientific, Inc. Silicon substrates are high-purity float-zone silicon with slight p-type conductivity of .001 S/cm. Impurity content for all materials used for which this information is available is tabulated above. All quartz substrates are cleaned in hydrofluoric acid (HF). All silicon substrates are cleaned using the method developed by the Radio Corporation of America (“RCA clean”). The recipes used for the substrate cleaning procedures are:

**HF-Cleaning**: Clean dust and residual organic content off quartz substrates by wiping with acetone, then ethanol, and then isopropanol. Etch surface layers off quartz plates by immersing in 5% aqueous hydrofluoric acid for 3 minutes.

**RCA Clean**: Clean dust and residual organic content off silicon substrates by sonicating in acetone for 30 minutes. This is done particularly to remove photoresist on the silicon, which is added during the cleaving process to prevent surface scratching. Soak in 5% HF for 30s. Soak in 70% H2O, 15% NH4OH, 15% H2O2 at 75°C for 10 minutes. Soak in 5% HF for 30s. Soak in 70% H2O, 15% HCl, 15% H2O2 (RCA-2) for 10 minutes. Soak in 5% HF for 30s. Soak again in RCA-2 for 10 minutes to grow surface oxide to reduce substrate conductivity.
Some comparison is made between films grown on bare substrates and those grown on Mo-coated substrates, since this constitutes the back electric contact for our final devices. Mo is deposited in a PVD Products multi-target sputter deposition chamber in 2 steps under 10 and 2 mTorr of Ar, respectively. The higher-pressure deposition creates a more pliable Mo layer for good adhesion to the substrate, while the lower-pressure deposition creates a dense, highly-conductive Mo layer.

### 3.2 Furnace setup

All sample annealing, as well as sulfurization in H\textsubscript{2}S, was performed in our lab’s home-built gas flow quartz tube furnace, capable of accessing temperatures up to 600°C and pressures between 5 mTorr and 0.5 Torr with tunable N\textsubscript{2}, Ar, H\textsubscript{2}, and H\textsubscript{2}S flows. Two heating zones allow independent control of temperature in the two halves of the furnace. A Hiden Analytical HPR-20 residual gas analyzer (RGA) samples the atmosphere in the furnace and gives gas composition data to sub-ppm sensitivity and mass resolution of 0.1 amu. A schematic of the furnace and attached RGA is shown below:

![Schematic of the furnace and RGA](image)

**Figure 3.1:** Schematic for H\textsubscript{2}S-capable gas-flow furnace. Gas flows through a quartz tube that is heated by insulating heating elements. Temperature, pressure, and gas composition are measured in real time.
3.2.1 RGA calibration

In order to achieve quantitative information on gas content from the RGA, I needed to calibrate the instrument. This is of particular importance for the experiments where I attempt to modulate carrier concentration by tuning the gas environment during annealing.

Calibration for N\textsubscript{2}, H\textsubscript{2}S, O\textsubscript{2}, and H\textsubscript{2} can be achieved using the built-in calibration tool in Hiden Analytical’s MASSoft software package. For this purpose, I use a calibrated mix of 3\% H\textsubscript{2}S, 1\% H\textsubscript{2}, and 96\% N\textsubscript{2}, obtained from Airgas. O\textsubscript{2} of 5N purity, also obtained from Airgas, is similarly used to calibrate the RGA for oxygen. Argon, and H\textsubscript{2}O are calibrated by analyzing ambient air and measuring the relative humidity.

Calibrating the tool for S\textsubscript{2} gas posed a significant challenge. S\textsubscript{2} forms in equilibrium with H\textsubscript{2}S and H\textsubscript{2} gases. At room temperature, the S\textsubscript{2} pressure is predicted to be extremely small, but becomes much larger as H\textsubscript{2}S is heated. In order to create gaseous S\textsubscript{2} in sufficient quantities to calibrate the instrument, and to prevent the S\textsubscript{2} from solidifying before it reaches the RGA, I devised the following apparatus (with the help of former lab member Dr. Katy Hartman):

A small chamber is filled with elemental sulfur chips, vacuumed down to $<100$ mTorr and filled with 120 Torr N\textsubscript{2} to provide an inert atmosphere. The chamber was then sealed shut and heated to the desired temperature (this procedure was repeated for several temperatures between 150-200°C) and allowed to reach equilibrium over the course of 24 hours. The chamber was then opened such that the gas inside was only allowed to leave through sealed tubes which were heated to a temperature of $>200$°C. This was to prevent sulfur condensation on the tube walls. These tubes then led directly to the RGA, which was itself heated to ~200°C. Thus, the sulfur gas never saw a temperature which was less than the chamber temperature. 200°C was chosen because this was the maximum temperature achievable by the surrounding pipes and RGA, and thus higher temperatures would likely have led to condensation of S\textsubscript{2} on the way to the RGA. A schematic is shown below.
In order to get quantitative data, I needed to de-convolute the signals of S₂, H₂O, and H₂. When being ionized by the RGA, S₂, S₃, etc. may crack into smaller fragments due to electron bombardment – in fact, the only measurable sulfur species were S and S₂. To quantify sulfur content, I must measure both the S and S₂. However, S presents at the same mass as O₂, which in turn partially cracks into single O atoms. H₂O also cracks into a combination of H₂O, OH, and O.

I deduced the cracking patterns by measuring the ratio of a given gas with its cracking products in a controlled gas environment. For example, to quantify the cracking pattern of oxygen, I flowed pure oxygen and measured the ratio of the O₂ signal (at mass 32) with the signal from O (at mass 16).

With these cracking patterns as well as the calibration patterns mentioned above, I was able to calculate the fraction of the RGA signal which is due only to sulfur. I wrote a script in MATLAB to do this, and it is able to output total sulfur content in any analyzed gas. However, because the heavier sulfur gas molecules (i.e., S₃, S₄, ..., S₈) were completely broken up by the RGA ionization process, this analysis cannot experimentally distinguish between different sulfur species. Thus, a “total sulfur” content was calculated by summing up all S atoms (i.e., total signal from S atoms plus 2x the total signal from S₂ molecules).

An illustration of this process, using a mass spectrometry readout from the RGA of an actual H₂S flow, is shown below.

**Figure 3.2:** Schematic for sulfur calibration setup. Sulfur is heated in a sealed, N₂-filled chamber at the desired temperature for 24 hours. This is repeated for several temperatures between 150-200°C. Vapor from the chamber was then sampled by the RGA through tubing which was heated to >200°C to prevent condensation. Blue boxes labeled “V” denote sealable valves.
Figure 3.3: Calculations for assessing sulfur content from RGA data. First, H₂O fragments are subtracted from the observed oxygen peak (m/z = 16). An oxygen cracking pattern is applied to calculate the ratio of O atoms to O₂ molecules, and signal due to O₂ is subtracted from the S peak (m/z = 32). Total S content is calculated by adding $S + 2*S₂$ partial pressures.

Now that I had measured the gaseous sulfur content above heated elemental sulfur, I needed to compare with predicted values to come up with a calibration curve for the RGA. The thermodynamic modelling program FactSage was used to calculate the predicted equilibrium pressure of S₂ above solid sulfur in an N₂ atmosphere of 120 Torr. I then compared the observed values with the expected values at each temperature that I analyzed to create the following calibration curve:
Figure 3.4: Calibration curve for S₂ gas analysis in a Hiden RGA system. Expected S content is generated from the thermodynamic modelling software FactSage. Observed S content is measured by the RGA. I wrote a MATLAB script to deconvolute the observed signal, which comes from a combination of Sₓ where x = 1—8, O, O₂, OH, and H₂O.

### 3.3 Single crystal preparation

I used SnS single crystals for carrier concentration studies during my contribution to the thesis work of Dr. Katy Hartman. These crystals were isolated from large-grained SnS samples grown by iodine-assisted vapor transport by Dr. Lee Burton of the Walsh group at U Bath, UK [39]. I confirmed that by a combination of cleaving and polishing I was able to isolate single crystal segments of these samples.

Smooth crystalline areas of the large-grained samples were identified visually. I then cut away any material outside this smooth area using a solvent-cleaned steel razor blade. The material surface often exhibited cracking or stray crystallites, and so the top crystal sheets were removed via exfoliation with Kapton tape. However, some surface cracking remained which presented as separate grains in x-ray diffractometry (XRD) scans (by showing multiple crystal orientations in a single sample). To confirm that these stray orientations were from surface cracking, I further polished all samples with 4000 grit polishing paper. This resulted in a single crystallographic orientation being present in XRD. In this case the (100) plane was parallel to the substrate, meaning that the flat graphite-like planes of SnS (basal planes) are parallel to the substrate. This process is summarized below with images:
Confirmation of single crystallinity was performed by XRD using a sequence of scans. XRD is described in more detail in Section 3.6. First, a quick 2-theta / omega coupled scan was performed along a single axis of the sample to confirm that only one orientation was present along that axis. However, this does not exclude the presence of a small number of stray crystallites which may be outside of the analyzing x-ray beam, or which may not have Bragg peaks along the axis which was scanned.

![Image of optical micrographs and X-ray diffraction patterns.](image)

**Figure 3.5**: Optical micrographs of large-grained SnS grown by iodine-assisted vapor transport, illustrating the steps for isolating a single crystal segment. From left to right, a) Sample as received from collaborator, b) sample after removing surrounding material and exfoliating surface. Cracking still present. c) Sample after surface polishing, removing all cracks.

**Figure 3.6**: X-ray diffraction patterns of SnS single-crystals at various stages of processing. a) A crystallite which has not been treated shows mostly a single orientation but exhibits many peaks. These stray peaks are reduced after b) cleaving and surface exfoliation, and completely eliminated after c) surface polishing, leaving only peaks from a single orientation.
Thus, further analysis was needed. A rocking curve was measured by tilting the sample back and forth by a few degrees while monitoring a single Bragg peak (in this case the (004) peak which presents at 31.9° 2-theta. If this peak presents more than once as the sample is tilted, this could indicate low-angle dislocations. The presence of only a single peak while rocking the sample helps confirm single-crystallinity.

A phi scan (in which the detector is swept in 360° around the sample while monitoring the (004) peak) was performed. Like the rocking curve scan, the presence of multiple peaks in this scan could indicate that the sample has low-angle dislocations, and the presence of only one peak rules out this possibility.

![Rocking curve and phi scans](image)

**Figure 3.7:** a) Rocking curve and b) phi scans of SnS single crystals taken via XRD to look for small angle grain boundaries and small crystallites along several axes of the sample. A single peak indicates that none such boundaries are detected.

Lastly, single-crystal diffraction patterns were taken using a Siemens/Bruker platform single-crystal diffractometer using a Bruker APEX CCD detector. Bruker software was used to identify all peaks present in the samples, and confirms that only peaks corresponding to a single crystal are observed. This instrument outputs a 3-D plot of the observed crystallographic axes overlaid on an image of the physical sample for easy viewing.
Figure 3.8: Single-crystal diffraction pattern of large-grained SnS samples showing the observed crystal planes overlaid on an image of the physical sample. The absence of any repeating planes indicates that this is indeed a single crystal of SnS.

Similar single crystals were then included in anneals at a variety of temperature and pressure setpoints to tune carrier concentration. These anneals and their results are described in Section 2.5.

3.4 Baseline thin film growth

Baseline samples using 4N pure feedstock are grown using our lab’s standard film deposition and processing steps. All baseline SnS films are grown on RCA-cleaned Si substrates (with the exception of samples for intrinsic defect studies, described in Section 4.1). Some Si substrates are also coated in Mo first for comparison to actual solar devices, which use a Mo back electrical contact.
3.4.1 Thermal evaporation of SnS

SnS is thermally evaporated at high vacuum – \( \sim 10^{-8} \) Torr – by heating a ceramic crucible containing 4N SnS powder to 600°C. The substrates are heated to approximately 240°C and rotate at 8 rpm to avoid overheating any one part of the apparatus. SnS is deposited at \( \sim 1.1 \) Å/s, for a final thickness of \( \sim 1.2 \) μm.

3.4.2 Annealing SnS films

All films are then annealed in the furnace (setup described above in Section 3.4) by placing the substrates on a cleaned, 4.5N pure quartz plate and placing this plate in the center of the heated zone of the furnace. The furnace, including all gas lines that will be used during the anneal, is pumped down to <12 mTorr pressure. It is then purged 3 times with N\(_2\), and after each time allowed to pump down to <1 Torr before being purged again. The furnace is then allowed to pump down to <12 mTorr before 4% H\(_2\)S in an N\(_2\) balance is allowed to flow through the furnace. By modulating the exhaust rate, the pressure inside the furnace is brought to 28 ± 0.5 Torr.

Several different annealing profiles are used in this study (this is in addition to the sulfurization recipes described below). The “standard” anneal is used to process the baseline samples and has been optimized, in addition to the SnS deposition and device building for our standard process, to achieve 3.88% NREL-certified efficiency [23].

A “grain growth” anneal was developed during prior work in our lab in order to optimize film morphology before attempting to tune carrier concentration in these films. This grain growth anneal is performed for several hours to allow the grain structure to fully mature.

As explained in Section 2.5.1, two primary hypotheses presented themselves for why hole concentration in SnS thin films seemed insensitive to annealing conditions. Morphological changes occurring during the grain growth anneal, particularly any densification of the films, could inhibit further point defect diffusion. In other words, it could be possible that the films start off with a large surface area-to-volume ratio which allows significant interaction with the H\(_2\)S atmosphere. However, upon densification, the bulk of the material could be shielded from interacting with H\(_2\)S gas, and thus carrier-generating point defects may not change appreciably over the course of the annealing experiment.

The second hypothesis was that extrinsic contamination, such as sodium, may be incorporating during the annealing process and obscuring any changes due to intrinsic defect concentration changes.
To account for the first hypothesis, I annealed different SnS thin films for a short period of time under two different conditions, which were predicted to result in very different carrier concentrations (using Kroeger-Vink modelling and prior work from our group as a guide). These anneals are referred to hereafter as “[p]-tuning A” and “[p]-tuning B”. This anneal had two purposes – first, tune the hole concentration [p], and second, induce a morphology change. Prior work from our group shows that morphological changes are clearly visible via SEM within several minutes of annealing, as demonstrated in Section 2.4.2.

I then subject these different films to an identical “grain growth anneal” in order to test the hypothesis that morphological changes in SnS “lock in” a carrier concentration, and inhibit further carrier concentration changes.

All of the anneals described above – “standard”, “grain growth”, “[p]-tuning A” and “[p]-tuning B” – are tabulated below.

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<th>Plateau Temp</th>
<th>Plateau Duration</th>
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<tbody>
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<td>60</td>
<td>Natural</td>
<td>28 Torr</td>
<td>4% H2S in N2</td>
</tr>
<tr>
<td>Grain growth</td>
<td>10 mins</td>
<td>450°C</td>
<td>180</td>
<td>Linear, 60 minutes</td>
<td>80 Torr</td>
<td>2% H2S, 2% H2 in N2</td>
</tr>
<tr>
<td>[p]-tuning A</td>
<td>10</td>
<td>400°C</td>
<td>10</td>
<td>Natural</td>
<td>80 Torr</td>
<td>0.365% H2S, 3.65% H2</td>
</tr>
<tr>
<td>[p]-tuning B</td>
<td>10</td>
<td>250°C</td>
<td>10</td>
<td>Natural</td>
<td>80 Torr</td>
<td>2% H2S, 2% H2 in N2</td>
</tr>
</tbody>
</table>

Table 3.2: Anneals used during this study. Standard and grain growth anneals were developed during prior work in our lab. [p]-tuning A and B anneals were developed for this study.

### 3.5 High-purity thin film growth

High-purity SnS is not available commercially – we currently utilize the highest-purity material available, which is 4N pure. Commercial Sn, by contrast, is available at 6N purity. As described in Section 2.4, there have been several cases of SnS synthesis via the reaction of Sn with either elemental sulfur or gaseous H2S. Commercial sulfur was only available at 5.5N purity, and so H2S gas (nominally metal-free) was considered to be a cleaner option.

#### 3.5.1 – Tin deposition

6N pure Sn shot was deposited on HF-etched quartz or RCA-cleaned Si substrates via thermal evaporation. The thermal evaporation was conducted at a shared-use facility. Therefore,
the evaporator chamber was conditioned before Sn deposition in order to reduce contamination from the chamber walls. 100-300nm of Ti was deposited as a gettering layer, followed by 100-300 nm of 5N purity Sn. The chamber was then vented, and substrates were loaded into the Sn-coated chamber on a metal substrate holder. HF-cleaned glass slides, on which substrates were mounted using Kapton tape, were used to attach the substrates to the sample holder, thus avoiding metal contacting the back of the substrates. Sn was deposited from an Al-coated W boat. 50nm of 6N Sn was pre-deposited on the walls of the chamber before the substrates were exposed to the Sn. Deposition rate was kept at 2 ± 0.2 angstroms/second, and a total of 300 ± 1 nm of Sn were deposited.

### 3.5.2 – Sulfurization

Several attempts were made to create phase-pure SnS by sulfurizing the deposited Sn films. All experiments were conducted in the furnace system described above. The reactive gas composition, total pressure, and time-temperature profiles for all experimental recipes are tabulated below:

<table>
<thead>
<tr>
<th>Sulfurization Recipe</th>
<th>Heating Duration</th>
<th>Plateau Temp</th>
<th>Plateau Duration</th>
<th>Cooling Duration</th>
<th>Total Pressure</th>
<th>Gas Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 mins</td>
<td>275°C</td>
<td>30</td>
<td>Natural</td>
<td>8 mTorr</td>
<td>Sulfur flakes heated to 315°C</td>
</tr>
<tr>
<td>2</td>
<td>10 mins</td>
<td>275°C</td>
<td>30</td>
<td>Natural</td>
<td>400 Torr</td>
<td>4% H₂S in N₂</td>
</tr>
<tr>
<td>3</td>
<td>120 mins</td>
<td>400°C</td>
<td>60 mins</td>
<td>Linear, 1hr</td>
<td>400 Torr</td>
<td>4% H₂S in N₂</td>
</tr>
<tr>
<td>4</td>
<td>120 mins</td>
<td>550°C</td>
<td>60 mins</td>
<td>Linear, 1hr</td>
<td>400 Torr</td>
<td>4% H₂S in N₂</td>
</tr>
</tbody>
</table>

Table 3.3: Parameters for different sulfurization recipes used during this study. Sn films were sulfurized in elemental S vapor as well as H₂S. It was found that H₂S sulfurization results in phase-pure films provided that films are heated for sufficient duration for a given temperature.

For each of these experiments, samples were loaded on an HF-cleaned, 4.5N pure quartz plate and placed in the heated zone of the furnace. I attempted to use two sulfur sources – heated elemental sulfur in low vacuum conditions, and 400 Torr of 4% H₂S in N₂ balance. The slow ramp-up in recipes 3-5 was used to prevent de-wetting of the Sn from the substrate surface, which was seen in recipe #2 with a short ramp-up. The goal was to form a small layer of SnS on the Sn surface before the Sn was allowed to reach its melting temperature of 231.9°C. Forming
such a “capping” layer to prevent movement of the underlying material during similar reactions has been shown to result in non-dewetted surfaces [74].

3.6 Phase analysis – XRD

Phase analysis was performed on a Rigaku SmartLab multi-purpose diffractometer using 2-theta / omega coupled scan mode. Peak identification was performed using Rigaku’s HighScore Plus software, as well as manual peak identification using published powder diffraction files (PDFs) for Sn, SnS, Sn₂S₃, and SnS₂.

X-ray diffraction works by shining a monochromatic beam of light at a crystalline or polycrystalline sample at a particular angle or range of angles (denoted \( \theta \)), and measuring the reflected light. As the beam passes into the sample, the repeating crystal planes act as partial reflection planes – at each plane, some light is transmitted while some is reflected.

Since the light is of a single wavelength, and since the crystal plane spacing is of a distance that is the same order as the light beam, constructive and destructive interference results. The majority of the time, light scatters off each plane in a way that causes phase interference, and very little light reaches the detector. However, at very particular angles – “Bragg angles”, reflections off of each subsequent crystal plane are in phase. The emitted radiation is thus enhanced and a signal can be observed by a detector. When this is the case it is said that the Bragg condition is satisfied.

The presence of Bragg angles gives information about the plane spacing \( d \) within a crystal for planes which are normal to the substrate (\( \theta = 0 \) refers to light passing parallel to the substrate). An illustration of when the Bragg condition is satisfied is shown below:
Figure 3.9: Satisfying the Bragg condition. \textbf{a)} An incoming x-ray beam is coming in at an angle $\theta$ which satisfies the Bragg condition for a crystal with a repeating atomic plane with spacing $d$ normal to the surface. Rays reflected off of each repeating plane leave the crystal surface in phase, generating an observable signal. \textbf{b)} An incoming x-ray beam is at an angle which does not satisfy the Bragg condition. Rays leaving the surface interfere destructively and do not generate an observable signal. Blue and green lines refer to the phase of the incoming light wave.

By simple trigonometry and wave optics, it can be seen that constructive interference occurs when the path length is increased by an integer number of wavelengths if the beam reflects off of a buried crystal plane as opposed to a crystal plane on the surface. Thus, if a strong reflection is picked up by the detector at a given angle of $\theta$, then we can assume constructive interference has occurred and we can relate the inter-plane spacing to the wavelength of light used, $\lambda$, and the angle $\theta$ at which the peak appears via Bragg’s Law:

$$n\lambda = 2dsin(\theta)$$

Where $n$ is an integer. We can simplify this by only considering the first harmonic and setting $n = 1$.

In the configuration shown above, it is assumed that the detector is placed above the sample at an angle equal to $\theta$. Measurements can be conducted in which the detector angle, $\omega$, is not equal to $\theta$. Similar reasoning can be used in this case. However, for all scans taken for this study, a 2-theta / omega coupled configuration is shown below, in which case as $\theta$ changes, the detector moves to keep $\omega = \theta$.

If many different crystal orientations are present, and at least some of each of these are normal to the substrate, then a signal may be observed at many different Bragg angles — one for each orientation. In single-crystalline samples analyzed for this study, it is desired that only one Bragg reflection presents itself — this indicates that only one crystallographic orientation is observed, which suggests the presence of only a single crystal. However, for polycrystalline samples also considered in this study, many peaks are present.

The exact location of these peaks in 2-theta space is a kind of “fingerprint” for a particular material. While a single peak may not be sufficient to identify a material, if many peaks are present in a polycrystalline sample then it is possible to confirm the presence of a given material. Moreover, if the material is phase-pure then only peaks corresponding to this
material should be present. Any other peaks can be linked to secondary phases or other materials present. This represents an efficient and sensitive method for identifying bulk and secondary phases in a material.

3.7 Morphology analysis – SEM

Morphology was assessed using secondary electron microscopy (SEM) imaging of samples on Zeiss Ultra55 and Zeiss Supra55VP Field Emission Scanning Electron Microscopes. Optimizing morphology is not within the scope of this project, and so morphology was simply assessed visually.

Electron microscopes focus a narrow beam of electrons on a sample and record electrons which re-emerge from the sample surface. These can be back-scattered electrons, which strike a sample, scatter elastically among the atoms within an interaction volume, and re-emerge. Back-scattered electrons probe a deeper interaction volume for a higher-energy incident electrons. They can also be secondary electrons, which are excited within the sample due to the initial electron beam. These secondary electrons are lower energy than the incoming beam, and so have a lower chance of escaping the material. Thus, secondary electrons typically probe an interaction volume that is much closer to the surface than back-scattered electrons.

3.8 Impurity analysis – XRF

In this study I attempt to use x-ray fluorescence (XRF) to quantify impurity concentrations in SnS thin film samples. XRF excites core electrons in samples using X-rays. Electrons are excited out of deep states, and higher-level electrons decay down to the now-empty core levels, producing x-rays. These x-rays have characteristic energies based on the atomic orbital levels. Since XRF probes deep electron levels, this technique does not distinguish significantly between atoms with different levels of bonding. Thus, atomic composition of a sample can be analyzed irrespective of bond structure. This process is illustrated below.
Figure 3.10: Illustration of XRF. Incoming x-rays excite core- or K-shell electrons to valence levels, resulting in several possible electronic relaxations from higher shells ($K_a$ and $K_b$ shown here). These relaxations can result in more vacant band states, which can be filled by secondary relaxations ($L_a$ shown here).

50 Watt palladium X-rays are focused on 3 targets to induce x-ray emission: low-energy (up to 8keV) radiation from pyrolytic graphite target, medium-energy (up to 16keV) radiation from Mo target, and high-energy (~35-40keV) radiation from Al$_2$O$_3$ target. X-rays from these targets are used to probe samples. High-energy X-rays can excite core levels from a larger range of atoms. Thus, the Al$_2$O$_3$ source can probe heavy elements that the other two X-ray sources cannot. However, more excited species means more secondary peaks, and thus a larger background. So, lower-energy X-rays allow for more accurate analysis of light elements.

3.9 Impurity analysis – SIMS

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis was performed by ION-TOF and Physical Electronics on their flagship nano-TOF II and TOF.SIMS 5 systems, respectively. Because of restrictions on tool use, only two samples could be sent for analysis during the course of this study – one 4N film, and one 6N film on a quartz substrate from recipe #3 described above. The latter sample was chosen because this run showed the best material quality, using lifetime as measured by TCSPC as a metric. Some data is taken as well on a 6N film grown by recipe #4. Because of the restrictions on tool use, only a subset of elements could be analyzed for this study.
TOF-SIMS operates by accelerating neutral atoms or atom clusters (typically Ar or C\textsubscript{60}, though other sputtering materials are used) towards a sample in order to blast away surface layers. A fraction of these surface atoms are ionized during this process and accelerated towards a detector. Due to random inelastic collisions during the initial sputtering of the sample, some ions with identical mass-to-charge ($m/z$) ratios are slightly spread out. Thus, all ions are fed through a focusing apparatus (PHI uses a reflectron, while nano-TOF uses their proprietary TRIFT system) to reduce spreading of ions with identical masses. These ions then impinge upon the detector. The amount of time it takes for a given ion to reach the detector is directly related to its $m/z$ ratio. Thus, by monitoring the number of ions striking the detector as a function of time following the initial bombardment of the sample, the $m/z$ ratio can be determined and the composition of the sample can be deduced. A simple schematic of this process is shown below.

Unlike some mass spectrometry systems, TOF-SIMS uses neutral species to bombard the sample. Thus, there is a low likelihood of doubly-ionizing any elements in the sample, and within small error we can assume that $z = I$ for all atoms or molecules reaching the detector, and thus the $m/z$ ratio can simply be taken as the atomic or molecular mass.

![Schematic of TOF-SIMS](image)

**Figure 3.11:** Schematic of TOF-SIMS. Neutral atoms or atom clusters bombard the sample surface and cause atoms to be ejected from the sample. A fraction of these are ionized in the process and accelerated towards a detector. They are filtered through a focusing system to reduce dispersion of ions with identical $m/z$ ratio.

### 3.10 Impurity analysis – ICP-MS

Inductively-coupled plasma mass spectrometry (ICP-MS) was conducted on an IsoProbe Multicollector Plasma Mass Spectrometer with the help of Rick Kayser of the lab of Prof. Ed Boyle at MIT.
ICP-MS, like SIMS, is a mass spectrometry system. It takes samples digested in acid, passes them through a nebulizer to convert species to gas phase, and ionizes the incoming species with an inductively-coupled plasma ionization source. The system uses a hexapole collision cell to reduce energy spread of the ion beam and fed into a magnetic sector mass analyzer where they impinge upon the detector – the IsoProbe tool used for these measurements uses Faraday cup detectors.

Samples were digested by placing a small drop of 6 molar, high-purity HCl on the SnS thin film surface and stirring it with a cleaned plastic pipette until the entire SnS thin film had dissolved. This acid drop was then pipetted into a new plastic centrifuge tube which had been rinsed 3 times with DI water. The samples were then diluted to the desired concentrations using the serial dilution method – a solution of approximately 2ppm and 200ppb Sn content by weight was made for each sample. DI water was used to dilute samples when necessary such that the total HCl content was 2% by volume. A HCl standard was prepared using similar plastic pipettes and beakerware at 2% by volume.

IsoProbe software was used to output raw data in counts/s which was processed in Excel.

### 3.11 Hall effect measurements

Hall Effect measurements can be used to determine carrier concentration in SnS thin film samples by measuring changes in current flow through a sample in response to an applied magnetic field [75]. Measurements were performed on a Keithley 4200 Semiconductor Characterization System.

Samples were prepared in the Van Der Pauw configuration [76], in which 4 contact pads are deposited in 1×1 mm² squares at the four corners of an 8×8 mm² sample. Contact pads consisted of 20nm Ti as an adhesion layer capped by 200 nm Au, both deposited by electron-beam evaporation in a Denton Explorer electron-beam evaporator.

Measurements were taken by sourcing a set current across a sample between diagonal contact pads. A magnetic field is then applied through the sample, orthogonal to the current flow. This field causes the sourced current to bend on its way through the sample, meaning that electrons will congregate on one end of the sample. The resulting voltage which is generated between the two remaining diagonal contact pads is measured. This is known as the Hall voltage $V_H$. The Hall voltage can be related to the carrier concentration through the following relationship:

$$V_H = \frac{I B}{[p] t e}$$

where $I$ is the current sourced through the sample, $t$ is the sample thickness, and $e$ is the elementary charge. This configuration is illustrated below:
Figure 3.12: Hall effect measurements taken in the Van Der Pauw configuration. A current $I$ is sourced through the sample while a magnetic field $B$ is supplied orthogonal to the current. The bending of the current pathway through the sample sets up a voltage $V_{H}$ which can be measured and related to carrier concentration.

3.12 Lifetime analysis – TCSPC

Minority-carrier lifetimes in 4N and 6N films were measured via time correlated single photon counting (TCSPC). Measurements were performed on a home-built system based on PicoQuant hardware. A laser pulse excites a sample, and the luminescence is measured by a highly sensitive avalanche photodiode. The timing of laser pulses are synced electronically with the sample luminescence so that the delay between excitation and luminescence in the sample can be accurately measured. A simple schematic of the setup is shown below.

Figure 3.13: Schematic of a TCSPC setup. A pulsed laser beam excites a sample with a pulsed laser, and the delay between excitation and photon emission from the sample is measured. Reproduced from PicoQuant literature [77].
This method exposes a sample to a short excitation pulse, and records the amount of time it takes for a photon to emit from the sample after excitation and reach a detector. By repeating this measurement a large number of times, a histogram can be generated for number of photons which present at a given time after absorption of the excitation pulse. A simple diagram is shown below to illustrate this process.

Figure 3.14: Data collection from TCSPC. a) Each pulse of a laser beam incident on a sample is recorded, as is the first photon emitted from the sample after each pulse. The delay between the two is measured. b) A histogram is constructed of how many photons present themselves a given amount of time after excitation. c) After many measurements, this histogram begins to resemble the photoluminescent decay curve of the entire sample.
Chapter 4
Results & Discussion

This study assesses the impact of point defects on SnS thin films for use in solar photovoltaics. In the first part of this study I measure the changes in carrier concentration in SnS films annealed at a variety of conditions. Contrary to expectations, the films did not conform to findings in the literature, which used Kroeger-Vink defect theory (described above in Section 2.5.1) and the assumption that the tin vacancy was the dominant intrinsic defect under S-rich conditions, at which these studies were performed. Rather, during this study it was found that any annealing caused the carrier concentration to increase greatly, but the actual annealing conditions did not seem to appreciably alter the resulting carrier concentration.

This led me to the hypothesis that the carrier concentration, and perhaps other properties as well, may be dominated by extrinsic, rather than intrinsic, contamination. As described above in Section 2.7, several extrinsic contaminants are predicted by DFT to form defect states in the bandgap of SnS [38]. Na, for instance, is highly abundant especially in biological tissue such as skin, and is predicted to act as a p-type dopant with negative formation enthalpy in SnS. It is possible that such contamination could obscure any changes in carrier concentration due to intrinsic defects.

The effects of extrinsic contamination were examined by growing SnS thin films by sulfurizing 6N pure Sn in high-purity H₂S gas, and comparing the impurity content and the minority-carrier lifetime of these films with our baseline process.

For details on the fabrication and characterization of all samples, refer to Section 3.

4.1 Intrinsic defect investigations

SnS single crystals and large-grained thin films used for this study do not conform to a simplistic Kroeger-Vink model of intrinsic defects. This led to two hypotheses: either the growth of cohesive grains inhibited further changes to carrier concentration, possibly by preventing diffusion of point defects through the material, or the increase in carrier concentration after annealing was due to incorporation of extrinsic contamination. Sodium forms a shallow p-type defect level with very low formation enthalpy in SnS. Moreover, sodium is present on all biological tissue as well as human breath and sweat. If any of this sodium made it to the sample...
before annealing, the low defect formation enthalpy would indicate that it should diffuse very quickly through the SnS at the elevated annealing temperatures and dope the material $p$-type.

To confirm or refute the first hypothesis, I perform a two-step annealing experiment described in Section 3.4.2. In a first anneal I attempt to tune carrier concentration. This first anneal has the ancillary benefit of inducing a morphology change, as evidenced by SEM images taken for the thesis of Dr. Katy Hartman. I then subject these films to a long anneal. If the hypothesis that an initial densification inhibits further changes to hole concentration holds true, then I would expect to see no further carrier concentration changes after this second anneal.

What I observed instead is that any anneal – regardless of annealing temperature, pressure, or even the initial deposition temperature for the thermally-evaporated films – results in approximately the same strong increase in carrier concentration as measured by Hall effect.

![Figure 4.1: Carrier concentrations for SnS thin films after short and long anneals. Films are annealed quickly to induce a change in carrier concentration as well as morphology – prior work shows that grains grow considerably within the first few minutes of annealing. Films are then annealed for a long period of time and re-measured. Carrier concentration rises upon annealing, but does not appear dependent upon the annealing conditions.](image)

It can be seen that any anneal, whether the short anneal with or without a further grain growth anneal, or even the grain growth anneal by itself, results in approximately the same
carrier concentration range of $\sim 5 \times 10^{16} - 1 \times 10^{17}$ cm$^{-3}$. It should be noted that this is approximately the same range as the carrier concentrations studies performed for the thesis of Dr. Hartman, in which SnS thin films were annealed to optimize morphology and then were annealed to change their carrier concentration.

The lack of any apparent dependence of the hole concentration on annealing parameters is in stark disagreement with prior literature, as well as with Kroeger-Vink defect theory if we assume that the $V_{\text{Sn}^{2+}}$ vacancy dominates. As described in Section 2.5.1, if a large range of defects are present in a sample, then solving defect chemistry equations for hole concentration becomes exceedingly complex.

These incongruencies between theory and experiment could be explained by a high degree of extrinsic contamination. As stated in Section 2.7.2, Na in particular is likely to form the $\text{Na}_{\text{Sn}}$ defect, which predicted to act as a $p$-type dopant and have negative formation enthalpy.

### 4.2 Phase analysis – XRD

Phase purity was established via x-ray diffraction (XRD). Many different sulfurization temperatures at a set H$_2$S pressure were tested for phase purity. It appears that within the temperature range analyzed, I am able to span the phase diagram of SnS from Sn-rich at the low-temperature end to S-rich at the high-temperature end. Details on SnS growth and the phase diagram are given in Section 2.4.

A low-temperature sulfurization was insufficient to fully react the Sn films during the duration of the anneal. Unreacted Sn manifests as peaks within the diffraction spectrum. Moderate temperatures of 400°C with a slow ramp-up and longer anneal duration resulted in phase-pure films on both quartz and silicon substrates.

High temperatures of 550°C resulted in over-sulfurization, and traces of Sn$_2$S$_3$ can be observed. This is surprising given that according to the predicted equilibrium phase diagram (see Section 2.4), over-sulfurized phases should not form for any of the setpoint conditions. One possible explanation involves the non-equilibrium annealing conditions. A constant “refreshing” of the sulfur atmosphere by constant gas flow could keep the available sulfur content high compared to a system with finite H$_2$S molecules, resulting in slight Sn$_2$S$_3$ formation. More analysis is required to understand the origin and location of Sn$_2$S$_3$ formation (i.e., if it is a thin surface layer or within the bulk). Further processing in a standard anneal (which has a lower temperature and sulfur pressure) reduced these films back to phase-pure SnS.

The ability to achieve phase-pure SnS with a variety of substrates and temperature conditions enhanced the flexibility of this work. While the goal of the study is to demonstrate higher minority-carrier lifetimes by using cleaner feedstock, I will eventually want to translate this work into a full device stack using the significant knowledge that our group has achieved for how to optimize materials and devices. Part of this optimization involves achieving good grain
Figure 4.2: XRD scans of 6N SnS films grown by sulfurizing Sn films under 400 Torr of 4% H₂S in N₂ at a variety of temperatures. **a)** For sulfurization temperatures of 250°C, not all of the material reacts and stray Sn peaks are observed. Sulfurization at 400°C yields phase-pure films on both **b)** quartz and **c)** silicon substrates. **d)** Sulfurization at 550°C results in over-sulfurized material, but **e)** this can be ameliorated by further putting these films through a standard anneal.
structure, low structural defect density, and low concentration of detrimental point defects. These can all be tuned by modulating processing temperature and pressure, and so it is desirable to be able to form SnS under a variety of temperatures and pressures.

4.3 Morphology analysis – SEM

Morphology was assessed via secondary ion microscopy (SEM). Images for the three of the best-performing samples are shown below – films grown under 400 Torr of 4% H₂S at 550°C on Si substrates, 400°C on quartz substrates, and 400°C on quartz/Mo substrates. A variety of morphologies are observed. Higher temperature showed a high nucleation density, with small, terrace-like grains dewetting from the substrate surface. Lower temperatures exhibit smooth grains, although the quartz substrate appears to have non-granular sections. These appear qualitatively like unreacted Sn, but no secondary phases appear via XRD and further analysis is necessary to deduce their composition. The Mo substrate has a morphology closest to the baseline films (shown in Section 2.4.2), though still displays some of the same non-granular material as the quartz substrate. Further study will focus on optimizing the morphology of these films, as the current films are likely unsuitable for full devices.

Figure 4.3: SEM micrographs of 6N SnS films sulfurized in 400Torr of 4% H₂S in N₂ balance. From left to right, a) 550°C on Si substrate, b) 400°C on Mo-coated quartz substrate, and c) 400°C on quartz substrate. These can be compared to our baseline film morphology. The dark area in figure a) is likely the Si substrate. The light grey area in figures b), c) is of unknown composition. Note that a clear cross-sectional view of c) could not be obtained.
4.4 **Impurity analysis – SIMS**

Impurity content for select elements was analyzed via mapping time-of-flight secondary ion mass spectrometry (TOF-SIMS). Baseline 4N films are compared against 6N films on quartz grown at 400°C and 6N films on Si grown at 550°C. Note that the 6N film on Si is the same sample which show lifetimes in the ns range via TCSPC, as seen in Section 4.7 (as well as the samples analyzed via SEM in Section 4.3). The 6N film on quartz is from the same sample set (and thus same processing conditions) as the 6N film on quartz/Mo which also shows ns-order lifetime (and which is also shown in Section 4.3).

All samples are O₂-sputtered to remove surface contamination and scanned using Bi⁺ primary ions at 30keV. Spot sizes vary - analysis shown for the 4N sample in a 400×400 μm² spot size, for 6N on quartz over a 250×250 μm² spot, and 6N on Si over a 20×20 μm² spot.

The results, shown as intensity plots within a given section of the film are shown below:

![Intensity plots](attachment:impurity_analysis.png)
Figure 4.4: SIMS analysis of 4N and 6N SnS films. Analysis of a) Al, Fe, La, and Na, and b) Ca, Si, K, and Sn. Almost all elements analyzed – Al, Fe, Na, Ca, Si, and K – have comparable or higher concentrations in 6N than 4N samples (Al in particular is much more prevalent in 6N films). La, by contrast, is much more prevalent in 4N films. Sn, which represents the bulk matrix, is shown for each sample for comparison. Results are uncalibrated, and scale bars across different elements should be taken as arbitrary.

This analysis constitutes a first attempt at SIMS data collection on 6N SnS, and so not all elements of interest could be analyzed for all samples during the course of this study. Fe, La and Ca could also not be analyzed in the 6N film on Si but are analyzed in the 4N and 6N on quartz samples. Moreover, this data is not quantified and therefore we can only make qualitative statements. A more complete analysis will be performed for future work, including the use of calibration standards. However, information can still be gleaned from the observed impurity content.

First, it is clear that that impurities in all films are not uniformly distributed. The distribution of impurities in semiconductors can alter their effect on the material. In multicrystalline silicon, both the total impurity content and the size and distribution of impurity-related defects dictates the resulting minority-carrier lifetime [78]–[80]. This suggests that point measurements such as traditional SIMS may not provide sufficient information alone, and rather a combination of spatially resolved measurements (such as the mapping SIMS used for this study) as well as bulk analysis methods are necessary to fully understand contamination in SnS.
It may be that, by analogy to silicon, lifetime is primarily affected by dispersed defects (which can affect a larger volume of the material than agglomerated precipitates).

Second, it can be seen that the 6N films are not uniformly cleaner than the 4N films. In particular, Al, Si, and perhaps Fe are more prevalent in the scanned region of 6N films than the scanned region of 4N films. This is contrary to the certificates of analysis shown at the start of Section 3. Al should be very sparse in both feedstocks, while Fe should be more prevalent in the 4N films. This could speak to faults in the deposition process for 6N films. Use of a shared-use thermal evaporator runs the risk of metal contamination despite the steps taken to prevent this. Further studies may focus on alternate growth methods for sulfurizing high-purity SnS.

Other elements – Na, K, and Ca – appear to have roughly the same concentrations in the regions analyzed from the 4N and 6N samples. They are distributed differently, with Na and K in particular appearing in the 4N sample in long streak marks. The source of these streaks is unknown, particularly because these samples were grown on RCA-cleaned silicon (the process for this is described in Section 3.1).

Without more information about the spatial distribution across the entire sample, I can only make limited inference on the impact of these defects. Because the lifetime improves between the 4N and 6N samples shown here, yet we see comparable or higher levels of Al, Fe, Na, Ca, Si, and K, these may not be limiting the minority-carrier lifetime at these concentrations. However, further study is necessary to assess the impurity content which is distributed homogeneously throughout the films (i.e., the impurity content between hot-spots). It could be that if the distribution of these impurities is different in the two materials, they could have different impacts on the minority-carrier lifetime.

One element in particular – La – appears at much higher concentrations in the 4N sample compared to the 6N sample (as expected according to the feedstock analysis). This element appears homogeneously distributed, and could be a candidate for future intentional contamination studies described in Section 5.

Lastly, it is important to consider the elements not analyzed by this method. Certain elements described as being potentially high-risk in Section 2.7.2 (Sb, As, Zn, and Cs) were not analyzed during this SIMS run. Further work will involve SIMS analysis on 4N and 6N samples for these particular elements.

4.5 Impurity analysis – ICP-MS

The impurity content in SnS samples could not be analyzed via ICP-MS as it was washed out by the background signal – many elements of interest even read negative values after background subtraction.
Due to the high sensitivity of the instrument, and to avoid severely contaminating the instrument with Sn, the highest Sn concentration allowed was set at 2ppm in HCl solution. If I am attempting to analyze impurities that are $<1$ ppm in the original SnS sample, then this would result in $\sim1$ ppt concentrations in solution. Though this is quite small, the instrument should feasibly be able to measure down to ppt.

It is hypothesized that since the sample volume dissolved was very small compared to the total amount of acid, it is possible trace impurities in the plastic centrifuge tubes contaminated the samples. These tubes were triple washed in DI water, but it is possible that the dilute acid was able to leach metal impurities from within the bulk of the tube.

Future studies will attempt to measure impurity content using ICP-MS in baseline and high-purity samples, using tubes that have been acid-leached for over 24 hours.

### 4.6 Impurity analysis – XRF

XRF was used to quantify impurity content in SnS. However, the system used exhibited a high background signal. This is partly due to a metal alloy sample holder which includes, among other metals, iron, cobalt, nickel, and copper. Combined with a lack of any sort of lead or other snout before the detector, this means that a large number of scattered photons are able to reach the detector. This results in the large background signal.

A first attempt at impurity content quantification via XRF was run on SnS powders of 4N purity used for baseline SnS thin film growth. For comparison, a film made from 6N purity feedstock was also measured. Data was inconclusive (except for an apparent reduction in Sb between 4N feedstock and 6N films) due to the high background signal, and further study was not attempted. Data is plotted below along with the background.

Note that this data does not include a background subtraction. As mentioned above, the background signal was high, and thus background-subtracted signals are not trustworthy, as small variations in the large metal background signal could show up as a false metal signal after subtraction. Thus the raw data is presented without background subtraction.
Figure 4.5: XRF measurements of SnS powder and films. 6N SnS thin films are compared to 4N Sn feedstock, as well as the background signal for the XRF tool used in this study. Peaks are identified with markers – black indicates peaks from Sn or S, green indicates peaks from substrate (Si) or Pd X-ray beam, and red indicates impurities. With the exception of Sb, which appears to have lower concentration in the “clean” films vs. “dirty” films, impurities could not be confidently detected. The background signal of many metals of interest, including Fe, Co, Ni, and Cu, is too high on account of the metal alloy sample holder.

4.7 Lifetime analysis – TCSPC

Time-correlated single photon counting (TCSPC) was used to measure minority-carrier lifetimes in 4N and 6N films. The instrument response function (IRF) represents the refreshing time for the detector, which has a decay on the order of under 200 ps. Any luminescence from the sample which is faster than the IRF (i.e. very short lifetime) will be convoluted with the decay signal from the initial excitation pulse.

4N films exhibit a decay signal which does not register above the IRF. This indicates that these baseline films have a lifetime less than ~200 ps. This is in agreement with ongoing work using THz spectroscopy [24] which indicates lifetimes in the 10s of ps.
6N films, by contrast, register a clear decay signal above the IRF. All decay curves are normalized against their maximum excitation and plotted below, along with double exponential fits for the minority-carrier lifetime.

![Graph of luminescent decay curves](image)

\[ \tau_{\text{IRF}} = 0.185 \pm 0.001 \text{ ns} \]
\[ \tau_{4\text{N}, 400^\circ\text{C}} = 0.187 \pm 0.002 \text{ ns} \]
\[ \tau_{1\text{N}, 400^\circ\text{C}} = 0.332 \pm 0.006 \text{ ns} ; \tau_{2\text{N}, 400^\circ\text{C}} = 2.548 \pm 0.033 \text{ ns} \]
\[ \tau_{1\text{N}, 550^\circ\text{C}} = 0.352 \pm 0.003 \text{ ns} ; \tau_{2\text{N}, 400^\circ\text{C}} = 2.497 \pm 0.038 \text{ ns} \]

**Figure 4.6:** Luminescent decay curves of excited carriers in SnS. 4N films exhibit decay on the order of the IRF, putting their carrier lifetime in the 10s of ps. By contrast, 6N films exhibit decay significantly above the IRF, with lifetimes up to several 100s or 1000s of ps.

A double exponential fit is used to separate out different decay mechanisms, as a single exponential does not fully fit the data. The initial steeper drop in intensity could be due to convolution with the IRF signal. It is also possible that this material exhibits an initial fast decay and slower decay, e.g. from surface and bulk recombination, respectively, but more work is necessary to better understand the origins of the observed luminescence signal.

This increase in observed minority-carrier lifetime constitutes a >1 order of magnitude improvement over baseline films. Though of course the samples are made by different methods as described above, and thus it could be argued that changes in surface recombination in the 4N films from thermal evaporation could be higher than 6N films made via sulfurization of Sn.

There are several reasons why this is unlikely to account for the higher signal. First, the observed morphology via SEM shows at best a grain structure in 6N films which is significantly more cracked than in baseline films. At worst, the morphology is characteristic of terraced growth, with irregular grains and a high degree of roughness.
As well, it is possible that this signal is due to secondary phases. Sn$_2$S$_3$ and SnS$_2$ could both form under sulfurizing conditions, even in small quantities. These materials are semiconductors with bandgaps of 1.09 eV and 2.24 eV, respectively, as calculated by DFT [39]. The Sn$_2$S$_3$ bandgap could interfere with the ~1.1 eV indirect transition in SnS, while sub-bandgap defect states in the large-bandgap Sn$_2$S$_3$ could be mistaken for any of the SnS transition levels.

As shown in Section 4.2, no Sn, Sn$_2$S$_3$ or SnS$_2$ is detected in any of the films measured. However, XRD analysis is not able to detect small concentrations of secondary phases, and further studies would use Raman spectroscopy or other methods to rule out the presence of secondary phases.

Similarly, trace Sn metal could be present in the grown SnS. However, this is unlikely to result in a falsely large observed lifetime. Sn itself does not luminesce. Additionally, the junction it forms with SnS can be predicted. We use a Sn work function of 4.4 eV and predicted band edge energies relative to vacuum for the (100) SnS plane (which is the dominant plane parallel to the substrate) of ~4.9/3.8 eV below vacuum for the valence band/conduction band, respectively [81]. According to the Schottky-Mott model for metal-semiconductor junctions, this would place the Sn work function directly in the middle of the SnS band. However, work by Bardeen et al. showed that metal-on-semiconductor junctions often pin at a particular level due to surface effects, thus shielding the bulk of the semiconductor material from “seeing” the metal beyond a few 10s of nm at the surface [82], which accounts for only a few % of the total semiconductor material volume for grains with dimensions of several hundred to thousand nm on a side, as can be seen via SEM images in Section 4.3. Thus, in this case Sn is not likely to deplete the majority of the SnS material. Ongoing work by our group indicates that most metals pin ~0.25 eV above the VB in SnS, in support of the Bardeen model.

The increase in carrier lifetime from 4N to 6N films is in agreement with the hypothesis that lifetime in SnS is substantially hampered by extrinsic contamination. This suggests that significant gains to material performance can be made simply by moving to cleaner feedstock and processing conditions.
Chapter 5

Conclusions & Outlook

In this study, I examined the intrinsically p-type semiconductor SnS as a potential absorber material in photovoltaic cells. I attempted to identify and assess the effects of point defects, both intrinsic and extrinsic, in SnS thin films.

Prior work showed that our SnS thin films changed carrier concentration upon annealing, but this carrier concentration then stayed nearly constant upon further annealing. This indicated a different mechanism than the simplistic model used in prior literature where SnS was dominated by just one defect – the tin vacancy. I considered two main hypotheses: 1) that grain growth in the SnS films inhibits point defect diffusivity through the material, thus hampering changes to carrier concentration after the initial densification, and 2) that the material was dominated by extrinsic defects caused by contamination.

I assessed the first hypothesis by first annealing for a short time at set temperature and pressure conditions. This anneal was meant to change the carrier concentration as well as promote film densification. A second anneal was then done to confirm or refute the hypothesis that carrier concentration changes were impeded following densification of SnS thin films. I found that regardless of which anneal was performed – whether just the first anneal, first and second anneal, or just the second anneal – all annealed SnS thin films exhibited similar carrier concentrations. No trend could be observed with annealing temperature or pressure for either anneal.

This further promoted the hypothesis that the material I was using was dominated by extrinsic contamination. Sodium is predicted to form defects with near-zero or negative formation enthalpy. Small amounts of sodium on the surface of an SnS sample would thus be quickly incorporated during high-temperature processing. Sodium is readily present on biological tissue as well as human sweat and saliva, and could easily be transferred to samples if special care is not taken.

This conclusion motivated further inquiry into the role of extrinsic point defects. For this study, minority-carrier lifetime was used as a metric for the electronic transport properties in SnS. Modelling work from our group indicates that an increase in minority-carrier lifetime of one to two orders of magnitude is required to achieve high-efficiency devices.
Films grown from 6N pure feedstock are grown by sulfurizing Sn thin films in H₂S. These are assessed for phase purity, crystallinity, morphology, and impurity content, and are compared against baseline samples grown from 4N pure feedstock.

6N films demonstrate a significant improvement in minority-carrier lifetime over 4N films, supporting the hypothesis that material quality is limited by contamination. However, it is yet unclear how much cleaner the 6N films actually are than 4N films. SIMS data indicates that 6N films are not uniformly cleaner than 4N films, with a reduction in only some elements. XRF, similarly, is only able to show a reduction in Sb. Future study will be necessary to fully analyze the impurity content of all elements in these films, and directly compare both the purity and the minority-carrier lifetime in films grown via the same method.

Within the bounds of this study, I demonstrate and quantify a lifetime improvement in thin films. However, the ultimate motivation for this work is to improve the efficiency of photovoltaic cells. Thus, the next logical step is to translate this purity work into improved devices. This is not as straightforward as attaching contacts to films from the present study – the films made for this study do not show morphology conducive to a high-efficiency solar cell, and rather have a large degree of irregularity, cracking, and roughness. However, it may be possible to leverage the techniques currently used by our lab to generate >3.8% efficient devices. For example, lacking commercial sources it may be possible to grow high-purity SnS for use as feedstock in a clean thermal evaporation system.

As well, I have demonstrated the value of material purity in general for SnS, but have not identified which specific defects are acting as lifetime-killing carrier traps.

With this work, I hope to motivate further inquiry into the role of contaminants in a variety of thin films. As stated in section 1.1, many nascent thin film materials suffer from poor transport properties. While significant work is being done to improve the intrinsic nature of these materials, relatively little is done to address the role of contamination.

Demonstrating a significant improvement in SnS by cleaning up the feedstock and processing can be seen as a test case for thin films in general. Understanding the minimum purity requirements to fabricate high-efficiency devices could unlock higher-efficiency devices for a variety of thin films. It could also provide guidelines for material manufacturers, who need to strike a balance between sufficient material purity, and the incremental costs of more and more purification.
References


