Investigations into the synthesis of ZnSnN$_2$ from SnO$_2$ thin-film conversion

A report
Submitted in partial fulfillment of the degree of
Bachelors of Science and Engineering

By:
Andrew E. Oriani

To:
Undergraduate Advisement Committee
Department of Physics
Case School of Engineering

Case Western Reserve University 2 May 2014
Abstract

II-IV-Nitrides have been proposed as a potential low-cost, low-toxicity alternative to commonly used III-V and II-IV-P\(_2\) materials. One such II-IV-N\(_2\) of particular interest is ZnSnN\(_2\). Recent experiments successfully growing ZnSnN\(_2\) have allowed for investigation into its structural, thermodynamic, and electronic properties. In order to better understand growth mechanics and thermodynamic properties of ZnSnN\(_2\), a novel method of annealing SnO\(_2\) thin-films in an NH\(_3\) environment modelled after the successful growth of ZnSnP\(_2\) has been proposed. Four experiments were conducted investigating the effects of varying temperature and partial pressure of NH\(_3\) and H\(_2\) on the compositional and structural properties of the SnO\(_2\) thin-film. The results of the experiments showed that SnO\(_2\) at 600°C favors reduction to Sn over conversion to ZnSnN\(_2\) in the presence of NH\(_3\), while at 550°C the cracking efficiency of NH\(_3\) is too low for conversion or reduction to occur. Results also showed SnO\(_2\) is highly susceptible to reduction in the presence of H\(_2\) at 550°C. Given these results, and the constraints of substrate integrity and ammonia cracking efficiency in the allowed temperature ranges, it has been shown that annealing of SnO\(_2\) is not a feasible method for ZnSnN\(_2\) thin-film growth.
I dedicate this thesis to Earl Snyder; the first person to open my mind and heart to the wonders and joys of science.

If what shone afar so grand
Turn to nothing, in thy hand
On again! The virtue lies
In the struggle, not the prize.

-Richard Monckton Milnes
Acknowledgements

I would first like to acknowledge the help and dedication of Dr. Kathleen Kash, who has constantly pushed me to pursue bigger and better things. I would also like to thank Eric Blanton, who has been my primary mentor in the development of this project. I would like to acknowledge the input of Dr. Tim Peshek, who initially proposed the project and has been an insightful source of discussion. I would like to thank Dr. Jonathan Cowan for his assistance in XRD measurements. I would like to also acknowledge Dr. Michael Martens and Dr. Ken Singer, who have given feedback as sitting members of my senior project committee. I also thank my friends who have supported by listening to my physics problems throughout the years; hopefully this will make everything about what I have been doing these four years more clear. Finally, I would like to thank my family, and my brother, Alex, who is both my foil but also a great source of inspiration and support in my life.
# Table of Contents

Chapter 1 | Introduction .................................................................................................................. 7  
1.1 Background ......................................................................................................................... 7  
1.2 Thin-Film Conversion .......................................................................................................... 8  
1.3 Thermodynamic Theory ..................................................................................................... 9  
1.3.1 ZnSnN₂ Thermodynamics ............................................................................................ 9  
1.3.2 SnO₂ Stability and Reduction ....................................................................................... 10  
1.4 Overview ............................................................................................................................. 14  

Chapter 2 | Experimental Design .................................................................................................... 15  
2.1 Description of Proposed Growth Technique ...................................................................... 15  
2.2 Growth Reactor .................................................................................................................. 15  
2.3 X-ray Diffraction and EDS Chemical Analysis .................................................................. 17  
2.3.1 Powder X-ray Diffraction ............................................................................................. 17  
2.3.2 EDS Chemical Analysis ................................................................................................. 18  
2.3.3 X-ray Diffraction and EDS Data Analysis .................................................................... 18  
2.4 Substrate Characterization and Handling ......................................................................... 19  
2.4.1 Substrate Characterization ........................................................................................... 19  
2.4.2 Substrate Handling ........................................................................................................ 21  

Chapter 3 | Growth Experiment Results ......................................................................................... 22  
3.1 Introduction ......................................................................................................................... 22  
3.2 Growths 1 and 2 .................................................................................................................. 22  
3.2.1 Growth 1 Results .......................................................................................................... 23  
3.2.2 Growth 2 Results .......................................................................................................... 25  
3.3 Growths 3 and 4 .................................................................................................................. 29
Chapter 1 | Introduction

1.1 Background

III-V direct band gap materials, namely InN and GaN, have become a staple of the opto-electronics industry, used in everything from high density optical storage and LED devices, to UV research lasers [Khan2006, Mills2008]. The rarity of Ga and In however have led to considerable research into new direct wide band-gap alternatives [Tolcin2013]. Punya et al. have suggested that heterovalent II-IV-N$_2$ compounds, where a group II-IV sublattice replaces the group III lattice site, may produce materials with tunable band-gaps ranging from the red to UV spectrum [Lambrecht2005, Punya2011]. Such properties make II-IV-N$_2$ materials a good low-cost, low-toxicity alternative to III-V nitride semiconductors. Previous studies into II-IV-N$_2$’s have yielded successful growth of ZnGeN$_2$ [Muanaye1970, Larson1974, Osinsky1992, Du2008, Peshe2008] and ZnSiN$_2$ [Endo1992, Cloitre2004] through a variety of methods, with successful growths dating back as early as 1970.

Until recently however little has been done concerning the study of ZnSnN$_2$. Theoretical studies of ZnSnN$_2$ have suggested a direct band-gap of ~2.02eV, making it a good candidate for further investigation [Lambrecht2005, Punya2011, Chen2013]. Calculations of the thermodynamic phase stability of single phase wurtzite ZnSnN$_2$ however have yielded varying and conflicting results. Successful synthesis of ZnSnN$_2$ along with competing binary phases by Quayle et al. using vapor-liquid-solid plasma-assisted growth [Quayle2013] as well as molecular beam epitaxy on YSZ and RF sputtering on sapphire and GaN substrates by Feldberg and Lahourcade
et al. have allowed for further verification and analysis of ZnSnN$_2$’s structural, electronic, [Feldberg2013, Lahourcade2013] and thermodynamic properties [Quayle2013].

1.2 Thin-Film Conversion

In continuing the study of ZnSnN$_2$ phase stability and growth, an alternative replacement reaction method for synthesis of ZnSnN$_2$ involving the annealing of a precursor thin film on glass in the presence of NH$_3$, modeled after successful conversion of a commercially grown SnO$_2$ thin film to ZnSnP$_2$ [Sansregret1981]. The SnO$_2$ substrate that is used was grown by the National Renewable Energy Labs (NREL) using CVD on Corning 7059® borosilicate glass [Corning, Li2008]. The experiment to be conducted is based on the solid state conversion of the SnO$_2$ substrate into ZnSnN$_2$. This reaction is dependent on the double replacement of the SnO$_2$’s oxygen with N$_2$ from NH$_3$. Invariably this pathway has a number of competing binary products that include Zn$_3$N$_2$ and Sn$_3$N$_4$ as well as ZnO and SnO. Because of the multitude of competing reaction kinetics, it is difficult to accurately predict the required conditions for SnO$_2$ conversion.

Sansregret, in producing ZnSnP$_2$ used PH$_3$ as his phosphorous source. By analogy, the experiments conducted used NH$_3$ for the attempted growth of ZnSnN$_2$. This difference in the group-V reactant species used in the growth of ZnSnN$_2$ constrains the range of temperature for which growth may occur, and substantially changes the thermodynamic kinetics of the solid state reaction in question. Mesrine et al. showed the temperature dependence of NH$_3$ cracking efficiency in MBE growth of GaN, with almost no NH$_3$ reactivity below 450°C, increasing exponentially to a peak cracking efficiency at or above ~600°C [Mesrine1997]. These data indicates that temperatures above 450°C are likely necessary to have any noticeable NH$_3$ reactivity, however the exact cracking efficiency is largely dependent on surface level kinetics.
that are a function of substrate composition and reactant partial pressures. To maximize the reactivity of \( \text{NH}_3 \) and allow for the investigation of \( \text{SnO}_2 \) reduction or conversion as a function of temperature, these experiments were conducted at 550°C and 600°C.

In growing \( \text{ZnSnP}_2 \), Sansregret also used \( \sim 8.5\% \, \text{H}_2 \) as part of his reactant gas mixture to maximize the \( \text{Zn} \) flow rate by reducing \( \text{ZnO} \) which may have formed at the surface of the \( \text{Zn} \) melt [Pankove1974]. While Sansregret did not report \( \text{SnO}_2 \) reduction in the presence of \( \text{H}_2 \) at 425°C, given our higher working temperatures, it is important to consider any reactions that may lead to \( \text{SnO}_2 \) reduction into liquid \( \text{Sn} \).

### 1.3 Thermodynamic Theory

#### 1.3.1 ZnSnN\(_2\) Thermodynamics

Given careful consideration, it is possible to predict \( \text{ZnSnN}_2 \) phase stability based on equilibrium thermodynamics. Phase stability of any alloy occurs when the individual phase, defined as a compositionally homogeneous and physically distinct part of the system, reaches equilibrium [Porter1981]. In the case of a single species, equilibrium is reached when the Gibbs free energy is minimized at constant temperature and pressure, or rather when the chemical potential of the species is zero. In binary systems, such as \( \text{SnO}_2 \), the most stable phase occurs when the total Gibbs free energy of the binary system is minimized. This process however is dependent on the relative molar concentrations of the two species present, and is illustrated below in Eq. 1.1, which is written in terms of the molar ratios \( (X_a \text{ and } X_b) \), the Gibbs free energy for the respective pure phases \( (G_a \text{ and } G_b) \), and the temperature dependent change in entropy due to mixing.

\[
G = X_a G_a + X_b G_b + RT (X_a \ln X_a + X_b \ln X_b)
\]  

\[ (1.1) \]
Eq. 1.1, however, is a gross oversimplification of the problem at hand, and assumes that the solution is ideal, with two species mixing to create a single binary phase. In reality there will be other structural and compositional phases present at equilibrium, i.e. the mixture at equilibrium will be a heterogeneous combination of pure, ordered, and disordered phases of the constituent compounds present. Another assumption of the above model is that the enthalpy and entropy of formation are well defined for all species involved which in the case of ZnSnN₂, are not well known to begin with.

Given the complexity of predicting the possible stable phases at equilibrium, analytical techniques do little to elucidate what molar ratios of constituent species will be needed to provide the desired stable ternary ZnSnN₂ phase. Furthermore, the above model does not take into account the influence of competing pseudo stable phases that may exist in non-equilibrium conditions. Given the limited capacity of analytic predictions or numerical models, experimentation is the best means to study the conditions necessary for the creation of ZnSnN₂. For this set of experiments these conditions include substrate temperature, gas composition and partial pressures of reactant species.

1.3.2 \textbf{SnO}_2 \textit{Stability and Reduction}

While ZnSnN₂ thermodynamics are impractical to solve analytically, the stability of SnO₂ under different conditions is not. The main concern at these higher temperatures is the integrity of the SnO₂ thin-film, since the solid state reaction under investigation requires a solid state replacement between SnO₂ and NH₃ to occur. Therefore, any reduction of the SnO₂ to SnO or liquid Sn would prove detrimental. As such there are several possible reduction pathways that may occur under our proposed growth conditions. These potential reduction reactions are listed as equations 1.2-1.5 below.
Chapter 1 | Introduction

\[ SnO_2 \rightarrow Sn(l) + O_2 \] (1.2)

\[ 2SnO_2 \rightarrow 2SnO(g) + O_2 \] (1.3)

\[ 2SnO_2 \rightarrow 2SnO(s) + O_2 \] (1.4)

\[ SnO_2 + 2H_2 \rightarrow Sn(l) + 2H_2O \] (1.5)

To elucidate the conditions conducive to reduction of SnO_2, it is necessary to know the equilibrium partial pressures of both O_2 and H_2O for Eqs. 1.2-1.5. These equilibrium calculations however are simply estimations of the relative stability of the substrate, and do not take into account non-equilibrium effects. For this reason, the calculation of the product and reactant equilibrium partial pressures is done assuming no competing interactions and only pure solutions.

To calculate the equilibrium partial pressures, equation 1.1 is written in terms of the Gibbs free energy taken at standard pressure (760 Torr) and reactant/product partial pressures. Taking equation 1.2 as an example, the expression for Gibbs free energy becomes

\[ G_{SnO_2}^\circ(T) = G_{Sn}^\circ(T) + G_{O_2}^\circ(T) + RT\ln\left(\frac{p_{O_2}}{p_0}\right) \] (1.6)

The Gibbs free energy is calculated using a cubic function fitted to empirically derived data for each species [Chase1998]. Details on this method are outlined in Appendix A. Table 1.1 shows different values for oxygen partial pressure at 550°C and 600°C. The data in table 1.1 indicates the inherent stability of SnO_2 at the growth temperatures of interest.

<table>
<thead>
<tr>
<th>( T )</th>
<th>( G_{SnO_2}^\circ(T) )</th>
<th>( G_{Sn}^\circ(T) )</th>
<th>( G_{O_2}^\circ(T) )</th>
<th>( P_{O_2}/P_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>550°C</td>
<td>-643.6kJ</td>
<td>-55.5kJ</td>
<td>-17.8kJ</td>
<td>4.6 \times 10^{-37}</td>
</tr>
<tr>
<td>600°C</td>
<td>-649.7kJ</td>
<td>-60.2kJ</td>
<td>-19kJ</td>
<td>5.9 \times 10^{-37}</td>
</tr>
</tbody>
</table>

Table 1.1: Partial pressures of O_2 at equilibrium for the reaction outlined in Eq. 1.6. The low equilibrium pressures of O_2 indicate that SnO_2 is stable at 550°C and 600°C. The existence of any ambient O_2 contamination would cause the reverse reaction to occur, increasing SnO_2 stability.
Sansregret reported that the presence of H$_2$ may assist in the flow rate of Zn vapor in the growth of ZnSnP$_2$ at 425°C. However given the elevated temperatures of these experiments, it is important to consider the effect of H$_2$ on SnO$_2$. Following the same method as Eq. 1.6, we are able to derive the following

$$G^0_{SnO_2}(T) + 2G^0_{H_2}(T) + 2RTln\left(\frac{P_{H_2}^0}{P_{H_2}}\right) = G^0_{Sn}(T) + 2G^0_{H_2O}(T) + 2RTln\left(\frac{P_{H_2O}^0}{P_{H_2O}}\right)$$

(1.7)

Using equation 1.7 we can solve for the equilibrium constant of the system, which can be written as

$$K_p(T) = \frac{P_{H_2O}^0}{P_{H_2}} = \exp\left(\frac{G^0_{SnO_2}(T) + 2G^0_{H_2}(T) - G^0_{Sn}(T) - 2G^0_{H_2O}(T)}{2RT}\right)$$

(1.8)

Plugging in known Gibbs free energies we find $K_p(550°C)=.68$ and $K_p(600°C)=.99$. With $K_p(T)$ known, it is possible to calculate the equilibrium pressure of H$_2$ required for the reduction of the SnO$_2$ substrate. The ambient pressure of H$_2$O, while small, is non-zero. Given the above values of $K$, the presence of any H$_2$ on the order of H$_2$O would reduce the SnO$_2$ substrate at temperatures between 550°C and 600°C. Since the ambient H$_2$O concentration is less than 1ppm, it would require much less than Sansregret’s 8.5% H$_2$ partial pressure to lead to the reduction of SnO$_2$ given our growth conditions. Figure 1.1 shows the temperature dependent relationship of Eq. 1.8. Although the equilibrium constant is higher at 550°C and 600°C, even at 425°C Sansregret should have seen evidence of reduction at 8.5% H$_2$ composition. This however indicates the approximate nature of equilibrium calculations in reference to the system in question, which is in a non-equilibrium state, and may indicate the presence of unforeseen kinetic barriers. Nonetheless, it is safe to expect SnO$_2$ to more easily reduce in the presence of H$_2$ than was seen by Sansregret.
The last decomposition pathway is the reduction of SnO₂ to the less stable oxidation state Sn(II)O which can exist either in a solid or gaseous phase. For the conversion of the SnO₂ to solid SnO, it is possible to calculate the O₂ pressure in equilibrium. Using the same formalism as Eq. 1.6, the values of Gibbs free energy and O₂ pressures for the reaction described by Eq. 1.2 are tabulated in Table 1.2 below. The equilibrium pressure of O₂ for Eq. 1.2 indicates that at the temperatures tested, SnO₂ is extremely stable, and is unlikely to form solid SnO. The partial pressure in terms of Gibbs free energy is

\[
P_{O_2} = \exp\left(\frac{2(g_{SnO_2}^0(T) - g_{SnO}^0(T)) - g_{O_2}^0(T)}{RT}\right) \tag{1.9}
\]

<table>
<thead>
<tr>
<th>(T)</th>
<th>(G_{SnO_2}^0(T))</th>
<th>(G_{SnO}^0(T))</th>
<th>(G_{O_2}^0(T))</th>
<th>(P_{O_2}/P_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550°C</td>
<td>-643.6kJ</td>
<td>-348.9kJ</td>
<td>-17.8kJ</td>
<td>(5.04 \times 10^{-37})</td>
</tr>
<tr>
<td>600°C</td>
<td>-649.7kJ</td>
<td>-354.6kJ</td>
<td>-19kJ</td>
<td>(6.38 \times 10^{-35})</td>
</tr>
</tbody>
</table>

Table 1.2: As with the reduction pathway described by Eq. 1.1, SnO₂ does not readily reduces to solid SnO as indicated by the exceedingly small O₂ equilibrium pressures.
For the decomposition of SnO$_2$ to gaseous SnO, since the ambient O$_2$ pressure is unknown, it is beneficial to look at the equilibrium constant $K_p$. Following the same methodology outline by Eq. 1.8, we arrive at the following equation for $K_p$.

$$K_p(T) = P_{\text{SnO}}^2P_{\text{O}_2} = \exp\left(\frac{2\left(g_{\text{SnO}_2}^0(T)-g_{\text{SnO}}^0(T)\right)}{RT}\right)$$  \hspace{1cm} (1.10)

The right half of the Eq. 1.9 is equal to the $K_p$ values listed in table 1.2, therefore $Kp(550^\circ \text{C}) = 5.04 \times 10^{-37}$ and $Kp(550^\circ \text{C}) = 6.38 \times 10^{-35}$. While the exact SnO pressure in the system cannot easily be predicted, if we set the ambient O$_2$ at 1ppm, we arrive at SnO pressures between $5.4 \times 10^{-13}$ and $6.1 \times 10^{-12}$ Torr for 550$^\circ$C and 600$^\circ$C respectively. This indicates that, while small, given time SnO$_2$ could reduce to SnO gas under the provided growth conditions. Combined with a constant flow of gas over the substrate, this process could be expedited; however quantifying this result would be exceedingly difficult to do.

### 1.4 Overview

While equilibrium thermodynamics give an idea of the possible effects of the SnO$_2$ conversion process, only experimentation and empirically derived results can confirm which reaction pathways are favorable for growth. Theoretical calculations indicate SnO$_2$’s inherent stability at 550$^\circ$C and 600$^\circ$C, while also showing SnO$_2$ high susceptibility to reduction into liquid Sn in the presence of H$_2$ at the proposed growth temperatures. As a means to study both ZnSnN$_2$ growth and the subsequent stability of SnO$_2$, experiments using NH$_3$ and H$_2$ were conducted. In total, four experiments were devised to investigate the feasibility of SnO$_2$ thin film annealing for ZnSnN$_2$ growth, two at 550$^\circ$C with and without H$_2$, and two at 600$^\circ$C with and without NH$_3$, with the final experiment being used to confirm SnO$_2$ stability at higher temperatures.
2.1 Description of Proposed Growth Technique

The experiments conducted in this thesis consisted of the annealing of a ~1.5μm thick SnO$_2$ thin-film deposited via CVD on glass in near atmospheric pressure conditions. Reactant species were provided via a constant flow of N$_2$, NH$_3$, H$_2$ and Zn vapor. The annealing took place inside of a single zone tube furnace. The SnO$_2$ films convert to ZnSnN$_2$ via a solid replacement reaction through the disassociation of the ammonia.

2.2 Growth Reactor

Figure 2.1: a.) A schematic and b.) image of the single zone tube furnace used for thin-film annealing, showing the primary hardware, feedthroughs, and locations of the Zn crucible and substrate.

The reactor used for the experiments discussed in this thesis and depicted in figure 2.1 was a single zone horizontal tube furnace. The reaction chamber consisted of an inner and outer quartz liner. The inner tube has dimensions of OD 34mm and ID 30mm x 500mm and spans the length of the reaction chamber. The outer tube has dimensions of OD 40mm and ID 36mm x 750mm, and is necked to 50mm at either end to allow for the attachment of double O-ring.
vacuum flanges made by Atomate®. Attached to these flanges were the 50mm 4-way crossings which sealed via KF vacuum hardware.

At the upstream end was an MKS® capacitance manometer with a 1-1000Torr range. The reactant gas flows were controlled via two MKS mass flow controllers. The high-purity (99.9997%) N₂ and (99.9995%) NH₃ gases were supplied from high pressure tanks, while H₂ was produced via a Chrysalis® hydrolysis reactor. All gases were passed through solid catalyst filter by Entegris® to reduce contaminant H₂O. Zn vapor was provided via a melt of high-purity (99.999%) Zn. The Zn was carefully rinsed in nitric acid prior to growth to reduce detrimental ZnO formation. Feedthroughs for thermocouples were also located at the upstream and downstream ends of the reaction chamber.

To insure constant pressure and flow control, an Alcatel® single stage rotary vane pump equipped with an MKS PID controlled butterfly valve was used, which provided pressure stability to within ±.1 Torr, which was greater in uncertainty than the average reactor pressure drop of ~.0026 Torr. Furthermore characterization of the flow dynamics yielded a Reynolds number of <10, indicating a laminar flow profile. Discussion on these design constraints can be found in Appendix B.

The Zn crucible and substrate holder were made out of high-purity graphite due to its inertness and high thermal conductivity. The two type-K thermocouples were located inside of the crucible and substrate holder, with the substrate thermocouple also being connected to the PID controlled furnace heater. To allow for control of Zn flow, the graphite crucible was made with a machined opening of 38 mm². With a partially open lid in place, Zn flow rates of between .037SCCM and .049SCCM were achieved. Explanation on these calculations may also be found
in appendix B. The Zn crucible was attached to a translational arm that allowed for the moving of the Zn melt into and out of the furnace’s central heating zone to maintain temperature.

2.3 X-ray Diffraction and EDS Chemical Analysis

2.3.1 Powder X-ray Diffraction

For structural analysis powder X-ray diffraction was used. The diffractometer used was a Scintag® X-1 powder X-ray diffraction system. The device was equipped with a CuKα ($\lambda=1.54050\,\text{Å}$) X-ray source. The diffractometer was setup to take grazing incidence measurements in order to improve the signal to noise of the of the thin-film’s diffracted peaks. This inherently caused a peak offset of $2\theta=15.999^\circ$ which was accounted for through manual offsetting.

The grazing incidence scans kept $\Omega$ (the X-ray incidence angle) fixed at $5^\circ$ to the substrate surface, while $\theta$ (the detector angle) was varied. Because Bragg-Brentano conditions weren’t met, the diffractometer caused artificial peak distortion at higher angles of $\theta$, limiting the effective range of $2\theta$ values to between $20^\circ$ and $60^\circ$. Nonetheless, for the investigation undertaken all relevant characteristic peaks lay in that range. It was decided to not take rocking measurements as to not artificially distort the data. As such, the substrate was left at $0^\circ$ inclination.

All scans were done with an accelerating potential of 44.5kV and a filament current of 39.5mA. Scans were made using $.02^\circ$ increments and an integration time of .2 seconds. The outgoing X-ray divergence and scatter slits were set to 1mm and 2mm, while the incoming scatter and receiving slits were set at .5mm and .3mm respectively.

Investigations into the diffractometer’s characteristic instrumental line-broadening yielded an inherent linewidth of $\Delta(2\theta)=.0038\text{Rad}$. This measurement was made using the...
characteristic $2\theta=31.7^\circ$ peak of a NIST SRM1976b sintered alumina standard [Kaiser2008]. Details on the characteristic linewidth calculations may be found in Appendix C.

2.3.2 EDS Chemical Analysis

Another method used to determine reacted substrate composition was X-ray chemical analysis via energy dispersive spectroscopy. These measurements were done on a Hitachi® S-4500 SEM equipped with a LN$_2$ cooled SiLi energy dispersive spectrometer. With this method, it is possible to measure chemical composition by measuring inner shell electron transition energies through X-ray excitations. For the measurements taken, the electron beam voltage was set at 30kV with a filament current of $17\mu$A. Scan times were set at 60 seconds.

To insure high resolution scans, the electron beam was calibrated to reduce astigmatic aberrations, allowing usable resolutions of $\sim1\mu$m. This allowed for high-resolution compositional measurements of surface level features.

All EDS measurements had a high amount of low-energy background caused by the presence of lighter elements, making measurements of oxygen and nitrogen containing species practically impossible. For this reason EDS was only used to confirm the presence of heavier compositional elements in surface level features.

2.3.3 X-ray Diffraction and EDS Data Analysis

All data and numerical analysis discussed in this thesis was done post-collection using MATLAB 2012b®. All X-ray diffraction figures, with the exception of C.2 and C.3, show data convolved with a 9$^{th}$ order Savitsky-Golay filter, which allowed for the reduction of high frequency noise without distorting sharp features or shifting of data. For numerical analysis, however only raw data was used to insure that there was no alterations of results due to post-processing.
EDS energy references were taken from the Section 1 of the X-ray Data Book [Thompson2001]. 2θ and intensity values were all taken from the Joint Committee on Powder Diffraction Standards’ (JCPDS) PDF 2-2000 database and are quoted by their JCPDS database numbers.

2.4 Substrate Characterization and Handling

2.4.1 Substrate Characterization

The substrate consists of a ~1.5μm thick CVD deposited SnO₂ thin-film on a .5mm thick Corning 7059® glass substrate. The SnO₂ was produced by the National Renewable Energy Laboratory (NREL) in Golden, Colorado for this investigation. While SnO₂ thin-films on borosilicate glass are widely available for commercial use and have been well characterized, our substrate had not had structural or compositional characterization done prior. As such, preliminary X-ray diffraction analysis was done to indicate the structure of the film. Figure 2.2 shows the results of grazing-incident X-ray diffraction.

![Unreacted SnO₂ I/I₀ vs 2θ](image)

Figure 2.2: Grazing incidence powder X-ray diffraction of unreacted SnO₂ on borosilicate glass
Figure 2.2 shows intensity as a function of $\theta$ overlaid with known SnO$_2$ peak intensities (JCPDS 01-0673). In the samples used the characteristic (I/I$_{o}$=100) peak is located at $2\theta$=51.76°, which corresponds to the [121] crystal plane of rutile SnO$_2$, as opposed to the usual characteristic [110] plane at $2\theta$=26.58°, which was also noted by Sansregret [Sansregret1981].

The presence of the [121] and [220] peaks, and the diminished intensity of the characteristic [110] plane peak, indicate that the SnO$_2$ thin-film exhibits a preferred orientation. Li et al. of NREL saw similar preferential orientation in CVD deposited SnO$_2$ thin-films on Corning 7059 glass [Li2008]. Their studies indicated that orientation was largely dependent on deposition temperature and fluorine doping levels in their precursor gas, with higher temperatures and fluorine leading to a preferred orientation of [200]. Spray Pyrolysis of SnO$_2$ on a variety of substrates revealed similar temperature dependent preferential orientation for rutile SnO$_2$ thin-films [Patil2011, Tatar2011].

With the above data it is possible to also investigate the average grain size for grains with [121] and [220] plane orientations. A simple way to do this, assuming there are no measurable non-uniform strain effects or grains larger than $\sim$2µm, is to use the Scherrer equation, which is written as

$$\tau = \frac{0.9 \lambda}{\beta \cos(\theta)} \quad (2.1)$$

where $\beta$ is the measured linewidth at half maximum (often denoted as $\Delta(2\theta)$) minus the instrumental line-broadening in radians, $\theta$ is the Bragg angle, and $\lambda$ is the wavelength of the X-ray source. A shape factor is also included, and is $\sim$0.9 for most materials including SnO$_2$. A numerical routine is used to closely approximate the peak shape and calculate $\Delta(2\theta)$ values. Subsequently, $\tau_{121}$= 60.8nm while $\tau_{220}$=63.40nm. These values for average grain size are also
consistent with those reported by Patil [Patil2011]. More information on peak shape approximations and $\Delta(2\theta)$ calculations are outlined in Appendix C.

2.4.2 Substrate Handling

Prior to each growth, the substrate was carefully cleaned using a multi-stage washing technique designed to remove potentially damaging organics while being safe on the SnO$_2$ surface. The wash consisted of 30 second acetone-methanol-isopropanol rinses with a 30 second deionized water rinse in between, followed by a final DI water rinse before being dried using lens paper. Special care was taken throughout to insure that natural or artificial organics don’t come into contact with the substrate. More information on contaminant reduction and reactor cleaning can be found in Appendix D.$^1$

---

$^1$ Standard substrate cleaning procedure avoids the use of an additional DI rinse between the solvent rinses.
Chapter 3 | Growth Experiment Results

3.1 Introduction

In total, four growths were conducted under varying temperature and reactant species compositions. The four experiments and their theoretical growth conditions are listed below in table 3.1.

<table>
<thead>
<tr>
<th>Growth</th>
<th>$T_s$(C)</th>
<th>$T_{Zn}$(C)</th>
<th>t(min)</th>
<th>$H_2/N_2/NH_3$ (SCCM)</th>
<th>$\kappa_{Zn}$ (SCCM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>550</td>
<td>511</td>
<td>360</td>
<td>0/15/45</td>
<td>.061</td>
</tr>
<tr>
<td>2</td>
<td>550</td>
<td>511</td>
<td>360</td>
<td>5/0/75</td>
<td>.061</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>511</td>
<td>360</td>
<td>0/15/45</td>
<td>.061</td>
</tr>
<tr>
<td>4</td>
<td>600</td>
<td>511</td>
<td>360</td>
<td>0/60/0</td>
<td>.061</td>
</tr>
</tbody>
</table>

Table 3.1: The theoretical values for substrate temperature $T_s$, Zn temperature $T_{Zn}$, duration $t$, the flow rates of the three reactant species, and the theoretical flow rate of Zn. The Zn temperature shown is the highest attainable temperature when $T_s=550^\circ C$, and is subsequently used for all four growths.

The conditions outlined in table 3.1 were created in part from prior ZnSnN$_2$ growth results, along with the theoretical framework laid out by the equilibrium thermodynamics discussed in Chapter 1. The following is an outline of the results for each set of experiments in the form of X-ray diffraction, EDS chemical analysis, and optical and scanning electron microscopy data.

3.2 Growths 1 and 2

Growths 1 and 2 were both conducted at 550°C for 360 minutes. The intent of these two growths was to determine NH$_3$ impingement and subsequent conversion/reduction of SnO$_2$ thin-films at 550°C, along with the effect of H$_2$ on conversion/reduction rates of SnO$_2$ thin-films, and to verify Sansregret’s observation of the effect of H$_2$ on Zn flow rates.
### 3.2.1 Growth 1 Results

![Image: A reflectance optical microscopy image taken at 50X magnification of growth 1 after annealing. The optically clear SnO$_2$ thin-film shows a polycrystalline surface morphology of dark brown/grey crystallites.](image)

The unreacted SnO$_2$ substrate was optically clear prior to growth. After growth 1, the substrate took on a translucent dark brown/grey film. Using reflectance optical microscopy, a polycrystalline thin-film made of dark, ~.3μm crystallites was seen. The reacted film layer was thin enough to allow some light transmittance, indicating that the reaction was confined to or near the surface.

To identify the composition of the reacted film, X-ray diffraction was conducted. Figure 3.2 shows the resulting structural and compositional makeup of the film determined by grazing incidence X-ray diffraction.
Figure 3.2: Grazing incidence powder X-ray diffraction pattern of the reacted SnO\textsubscript{2} thin-film in growth 1.

The above indicates that at 550°C in an NH\textsubscript{3} rich environment SnO\textsubscript{2} remains intact. The data aligns well with the SnO\textsubscript{2} reference (JCPDS 01-0673). The characteristic 2\(\theta\) peak shows shifting from 51.76° to 51.74°, indicating that uniform strain was introduced into the [121] direction, causing the uniform distortion of the [121] interplanar spacing. This, however cannot be proven definitely as 2\(\theta\) peak shifts <.5° are within the uncertainty of the instrument, and would require more careful calibration to be justified as being a product of induced homogeneous strain.

Annealing the film also caused a change in the \(\Delta(2\theta)\) of the 2\(\theta\)=51.74° peak. The annealed film’s new \(\Delta(2\theta)=.0058\)Rad, corresponding to an average grain size of \(\tau_{121}=76.9\)nm, a result consistent with those reported by Kose \textit{et al.} and Patil \textit{et al.} who found increases in grain sizes upwards of 30\% for \(T>550^\circ\text{C}\) [Patil2011, Kose2013].
3.2.2 Growth 2 Results

Figure 3.3: A reflectance optical microscopy image taken at 50X magnification of growth 2 after annealing. The optically clear SnO$_2$ thin-film shows a polycrystalline surface morphology of varied crystallites. Under normal lighting the yellow regions would appear metallic, while the grey regions would appear brown.grey.

As with growth 1, growth 2 was conducted at 550°C for 360 minutes; however growth 2 saw the inclusion of ~6.6% H$_2$ gas by composition. The resulting reacted film had a metallic sheen while remaining optically translucent; indicating again that the reaction was confined to a very thin layer near the surface. Optical reflectance microscopy, shown in figure 3.3 above, revealed a polycrystalline surface with crystallites ~.4µm in size.

To identify the composition and structure of the annealed film in growth 2, grazing-incident X-ray diffraction was conducted. The resulting I/I$_0$ vs 2θ plot is depicted in figure 3.4 below.
Figure 3.4: Grazing incidence powder X-ray diffraction pattern of the reacted SnO$_2$ thin-film in growth 2 showing the presence of Sn, ZnO, and unconverted SnO$_2$.

The X-ray diffraction pattern depicted in figure 3.4 indicates a partial reduction of the SnO$_2$ thin-film into an ad-hoc combination of Sn (JCPDS 04-0673), ZnO (JCPDS 03-0888) and unreacted SnO$_2$ (JCPDS 01-0673). The noticeable amount of ZnO could indicate contamination, however in the presence of H$_2$, ZnO should be less prevalent in the Zn melt, the primary source for ZnO contamination. This is supported by the resulting higher flow rates reported by Sansregret with ~8.5% H$_2$ and is likely due to the presence of surface level ZnO which acts to reduce the vapor pressure of the melt by increasing surface tension [Pankove1974, Sansregret1980]. This notion is also supported by the slight increase in measured flow rates between growth 1 and 2 (.043SCCM vs .044SCCM). With this in mind, ZnO likely formed as a byproduct of SnO$_2$ reduction via an increase in O$_2$ partial pressure.

The additional Sn peaks support the optical microscopy, which revealed a surface with a metallic luster interspersed with regions of crystallites of similar appearance to those in growth 1 which were determined to be SnO$_2$. This data also supports equilibrium thermodynamic
calculations that indicated an equilibrium constant $K_p(550°C)=.68$ for the reduction of SnO$_2$ in an H$_2$ environment at 550°C.

To learn more about the surface morphology and presence of liquid Sn, scanning electron microscopy was done. Figure 3.5 shows an SEM image taken at 4000X magnification.

![SEM image](image_url)

Figure 3.5: An SEM image taken at 4000X magnification showing the surface morphology of the SnO$_2$ thin-film after growth 2. The image shows a non-ordered surface morphology with ~1μm balls of Sn.

The surface shows no ordering, with numerous metallic spheres dispersed across the surface. The spheres are thought to be pure Sn, and are likely a result of liquid Sn’s poor wetting characteristics, supporting the notion set out by equilibrium thermodynamics indicating SnO$_2$ reducibility to liquid Sn in an H$_2$ environment.

To further confirm this hypothesis, electron dispersive spectroscopy, depicted below in figure 3.6, was also done on the reacted film following growth 2.
Figure 3.6: EDS plot showing emitted X-ray energies for the reacted growth 2 SnO$_2$ film overlayed with the known K and L transition energies for Sn and Zn.

The electron dispersive spectroscopy aligns well with both X-ray diffraction data and SEM images, showing a high concentration of Sn along with some Zn. The estimated percent composition of Zn and Sn are given in table 3.2.

<table>
<thead>
<tr>
<th>Element</th>
<th>Line</th>
<th>Weight %</th>
<th>Weight % Error</th>
<th>Atom %</th>
<th>Atom % Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>K</td>
<td>31.15</td>
<td>+/- 2.76</td>
<td>45.10</td>
<td>+/- 3.99</td>
</tr>
<tr>
<td>Sn</td>
<td>L</td>
<td>68.85</td>
<td>+/- 3.57</td>
<td>54.90</td>
<td>+/- 2.85</td>
</tr>
</tbody>
</table>

Table 3.2: EDS derived percent composition values for Zn and Sn for growth 2.

This, combined with the lower peak intensities of the characteristic $2\theta$=51.72 for the SnO$_2$ [121] plane all indicate that the reduction reaction predicted by Eq. 1.5 likely took place.
3.3 Growths 3 and 4

Growth 3 and 4 were conducted at identical temperatures of $T_s=600^\circ C$ for 360 minutes. The objective of these experiments was to determine the effect high temperature had on NH$_3$ cracking efficiency and subsequent reactivity with SnO$_2$ as well as the long-term high-temperature stability of the SnO$_2$ substrate as predicted by equilibrium thermodynamics.

3.3.1 Growth 3 Results

Growth 3 sought to investigate the effect temperature had on NH$_3$ reactivity and the subsequent conversion/reduction of the SnO$_2$ thin-film after growth 3. The reacted thin-film showed a bright metallic, almost mirror like lusted with large metallic spheres ($<100\mu m$) dispersed across the surface. A 50X optical reflectance microscopy image is depicted below in figure 3.7.

![Figure 3.7: 50X optical reflectance microscopy image of the reacted SnO$_2$ thin-film following growth 3. The surface morphology shows regions of flat metallic regions (yellow) $\sim$5-10$\mu m$ in size, and smaller darker areas of $\sim$2$\mu m$ in size.](image)
While visual inspection suggested a converted film similar to that of growth 2, optical microscopy showed a very different microscopic surface morphology covered in large relatively flat regions of metal interspersed with darker areas.

To learn more about the composition and structure of the converted thin-film, X-ray diffraction measurements were taken, with the results depicted below in figure 3.8.

![Growth #3 \(I/I_o\) vs 2\(\theta\)](image)

**Figure 3.8:** Grazing incidence powder X-ray diffraction pattern of the reacted SnO\(_2\) thin-film in growth 3 showing the presence of Sn. Unlike growth 2, growth 3 shows no sign of unconverted SnO\(_2\).

The X-ray diffraction data shows that the SnO\(_2\) thin-film has been completely replaced with pure Sn. This drastic departure from the results of growth 1, which only differed in temperature, shows that NH\(_3\) cracking efficiency is much higher at 600°C, which had been predicted by Mesrine *et al.* to be the peak of NH\(_3\) reactivity in MBE growth of GaN [Mesrine1997]. The only peak unaccounted for was at 2\(\theta\)=28.86°, which didn’t closely match any of the possible product species.

To better understand the surface morphology, SEM images were taken at 4000X and 30,000X and are displayed in figure 3.9.
Figure 3.9: a.) A 4000X SEM image of the reduced surface of growth 3 showing dark regions (A) and light regions (B). b.) depicts a 30000X SEM image of growth 3, zooming into an interface between regions A and B.

The two images show varying aspects of the surface morphology. At lower magnifications the surface appears perfectly smooth, however at 4000X spheres similar to those seen in growth 2 appear. Likewise, Fig 3.9b shows that the flat sheets of metal are not mixed with the dark regions, but rather sit on top, with little to no wetting occurring at the A/B interfaces. All of these results corroborate with the X-ray diffraction data; however there is no good indication from either as to what region A is composed of. Based on the analysis so far, there is a strong indication that A is in fact the underlying glass. To further this point, EDS was done independently on both regions in Fig. 3.9b. The results are given in Fig. 3.10 below.
Figure 3.10: EDS of the reacted SnO$_2$ thin-film after growth 3 overlayed with the known K and L transition energies for Sn, Ca, and Si.

For region A, EDS shows almost no Sn, but rather noticeable amounts of Si and Ca. The presence of silicon and calcium are indicative of the soda-lime glass substrate, suggesting that the dark regions are in fact glass. This is bolstered again by the lack of Si containing compounds in the X-ray diffraction data, indicating that Si containing compounds must be in an amorphous phase. Similarly, region B has a strong Sn signal, confirming visual analysis and X-ray diffraction data. The presence of the exposed underlying amorphous Si/Ca containing substrate could also explain the large underlying noise seen in growth 3 X-ray diffraction data. The percent compositions of the two regions as measured by EDS are listed in tables 3.3 and 3.4 below.
Region A

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight</th>
<th>Weight Error</th>
<th>Atom %</th>
<th>Atom Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si K</td>
<td>54.08</td>
<td>+/- 1.96</td>
<td>73.15</td>
<td>+/- 2.65</td>
</tr>
<tr>
<td>Ca K</td>
<td>16.08</td>
<td>+/- 1.41</td>
<td>15.24</td>
<td>+/- 1.34</td>
</tr>
<tr>
<td>Zn K</td>
<td>7.88</td>
<td>+/- 2.29</td>
<td>4.58</td>
<td>+/- 1.33</td>
</tr>
<tr>
<td>Sn L</td>
<td>21.96</td>
<td>+/- 3.67</td>
<td>7.03</td>
<td>+/- 1.18</td>
</tr>
</tbody>
</table>

Table 3.2: EDS derived percent composition values for Si and Ca in region A for growth 3.

Region B

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight</th>
<th>Weight Error</th>
<th>Atom %</th>
<th>Atom Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn K</td>
<td>2.36</td>
<td>+/- 0.77</td>
<td>4.20</td>
<td>+/- 1.37</td>
</tr>
<tr>
<td>Sn L</td>
<td>97.64</td>
<td>+/- 2.91</td>
<td>95.80</td>
<td>+/- 2.86</td>
</tr>
</tbody>
</table>

Table 3.2: EDS derived percent composition values for Zn and Sn for region B of growth 3.
3.3.2 Growth 4 Results

Growth 4 was designed to test the predicted stability of SnO$_2$ at 600°C but to also determine if the results of growth 3 weren’t induced via a mechanism other than NH$_3$ reactivity. To do this, growth 4 completely removed the presence of any NH$_3$ or H$_2$ gas. Instead, 60SCCM of N$_2$ were flowed in order to maintain the same Zn partial pressure as growth 3.

Optical reflectance microscopy, depicted below in figure 3.11 revealed a surface morphology similar to that seen in growth 1.

Figure 3.11: A Figure 3.7: 50X optical reflectance microscopy image of the reacted SnO$_2$ thin-film following growth 4. The surface morphology appears similar to that of growth 1, with crystallites being slightly larger at ~7-1μm in size. The film is also less transluscent than growth 1, and shows slightly more compositional variation.

The surface is covered in a polycrystalline film with crystallites on the order of ~1μm in size. The surface also shows more compositional variation than growth 1, with noticeable amounts of metallic crystallites. All of this indicates that growth 4’s SnO$_2$ film underwent slight but noticeable conversion/reduction. The X-ray diffraction data, depicted in figure 3.11, corroborates the qualitative analysis by showing the presence of some Sn.
Figure 3.12: Grazing-incidence powder X-ray diffraction pattern of the reacted SnO₂ thin-film in growth 4 with relevant peak locations for Sn and SnO₂. Like growth 1, the film remained stable, however, the increased intensity of Sn peaks at \(2\theta=43.82^\circ\) and \(2\theta=44.86^\circ\) indicate some SnO₂ reduction.

Like growth 1, X-ray diffraction shows a strong characteristic SnO₂ peak at \(2\theta=51.7^\circ\), however the increased peak intensity for \(2\theta=43.82^\circ\) and \(2\theta=44.86^\circ\) hint at some SnO₂ reduction.

The characteristic [121] peak from sample 4 also shows a similar \(2\theta\) shift to that of growth 1. Similarly, \(\Delta(2\theta)=.0057\text{Rad}\), which corresponds to an average grain size of 79.98nm, which is also consistent with previous SnO₂ annealing studies.
Chapter 4 | Discussion

4.1 Introduction

Although the goal of the aforementioned investigation was to successfully grow ZnSnN$_2$, the results, which failed to produce any sign of a binary or ternary nitride, has proven successful in confirming several theoretical observations, as well as corroborating with previous studies into the effects of annealing on SnO$_2$ thin-film properties. This discussion will address several discrepancies in the data, namely the formation of ZnO in growth 2 and the reduction of SnO$_2$ in growth 4.

4.2 ZnO Equilibrium Thermodynamics

4.2.1 ZnO Formation by O$_2$

Growth 2 did much to elucidate the equilibrium thermodynamics of SnO$_2$ in the presence of H$_2$, however the subsequent reduction of SnO$_2$ in the presence of H$_2$ seemed to coincide with the noticeable formation of crystalline ZnO. Given that a binary Zn species failed to show up in XRD data at any other point in the investigation, it is of interest to address the theoretical framework behind ZnO’s formation in growth 2. The main pathway for formation of solid ZnO is written below as

\[
2\text{Zn}(g) + \text{O}_2(g) = 2\text{ZnO}(s)
\] (4.1)

We can subsequently write 4.1 in terms of Gibbs free energy

\[
2G^0_{\text{Zn}}(T) + G^0_{\text{O}_2}(T) + 2RT\ln\left(\frac{P_{\text{Zn}}}{P_0}\right) + RT\ln\left(\frac{P_{\text{O}_2}}{P_0}\right) = 2G^0_{\text{ZnO}}(T)
\] (4.2)

From equation 4.2 it is possible to derive the rate constant $K_p(T)$, which is simply

\[
K_p(T) = P^2_{\text{Zn}}P_{\text{O}_2} = \exp\left(\frac{2G^0_{\text{ZnO}}(T) - 2G^0_{\text{Zn}}(T) - G^0_{\text{O}_2}(T)}{RT}\right)
\] (4.3)
From this we can calculate the rate constant at 550°C, which gives us $aK_p(550°C) = 3.42 \times 10^{-39}$. With this value in mind, we can calculate what the equilibrium $O_2$ pressure has to be given the known Zn pressure in the reactor. The Zn pressure can be calculated as follows

$$P_{Zn}^* = \frac{\kappa_{Zn}}{\kappa_{total}} P_{reactor} \quad (4.4)$$

where $\kappa_{Zn}$ and $\kappa_{total}$ are the flow rates of Zn and the total flow rate respectively, and $P_{reactor}$ is the ambient pressure in the growth chamber. Knowing those values, we arrive at $P_{Zn} = 4.2$ Torr. From the left half of equation 4.3, we can derive the equilibrium $O_2$ pressure $P_{O_2} = 1.94 \times 10^{-38}$ Torr.

Given the incredibly small equilibrium pressure of oxygen required to produce ZnO, it is reasonable to believe that the conditions were conducive for the reaction to progress in the forward direction. In fact, given the equilibrium pressures of $O_2$ in the decomposition of SnO$_2$ to Sn at 550°C, ZnO is likely always forming, however the conditions of growth 2 likely allowed the rate of ZnO formation to be a dominant factor. Therefore, the equilibrium thermodynamics agree with the results of growth 2, indicating that ZnO did not likely form as a contaminant but rather due to favorable kinetics.

### 4.2.2 ZnO Formation by H$_2$O

Another pathway common for ZnO formation is the interaction of Zn and H$_2$O. Anthrop and Searcy reported that the presence of H$_2$O vastly affected the rate of ZnO formation in equilibrium [Anthrop1964]. The pathway Anthrop was referring to can be written as

$$Zn(g) + H_2O(g) \leftrightarrow ZnO(s) + H_2(g) \quad (4.5)$$

By writing equation 4.5 in terms of Gibbs free energy, it is possible to solve for the equilibrium constant $K_p$, which is dependent on the relative pressures of H$_2$, H$_2$O and Zn at equilibrium. The equation for $K_p$ can be written as
From 4.6 we can solve for $K_p(T)$ at 550°C. In doing so, we arrive at $K_p(550°C) = 4.08 \times 10^{-7}$. Since the pressure of Zn and H$_2$ are known, it is now possible to calculate the required pressure of H$_2$O at equilibrium, in doing so we find an equilibrium pressure of H$_2$O at 550°C to be $3.88 \times 10^7$ Torr.

The H$_2$O pressure at equilibrium is much higher than the pressure of the system, indicating that, in the presence of H$_2$, ZnO formation is unlikely to occur due to the interaction between Zn and H$_2$O, which is consistent with Anthrop’s findings that ZnO formation is most favorable in environments with extremely low H$_2$ ambient pressures.

4.3 Sn Formation in Growth 4

Another discrepancy in the data is the formation of pure Sn in growth 4. The equilibrium thermodynamics indicate that of all the reduction pathways for SnO$_2$ at 600°C, the decomposition of SnO$_2$ to SnO and O$_2$ gas is the most favorable. In growth 4, however, this is not what was seen. Instead, a small amount of pure Sn was formed.

There are only two reduction pathways that produce pure Sn as a product in equilibrium. The first is the reduction of SnO$_2$ to liquid Sn and O$_2$. This pathway, however, is not favorable, as the equilibrium pressure of O$_2$ is so small that the introduction of any O$_2$ contaminants would lead to a reverse reaction. The second pathway is the SnO$_2$ and H$_2$ to H$_2$O and liquid Sn. At 600°C the equilibrium constant is close to 1, meaning that a small ambient H$_2$O pressure would lead to reduction with any inclusion of H$_2$. It is therefore not unreasonable to presume that H$_2$ contamination may have been the cause, especially in an otherwise inert environment. The potential source was likely ambient H$_2$ in the gas feedline between the H$_2$ generator and the reactor.
Chapter 5 | Conclusion

Through the four aforementioned experiments, it has been shown that annealing of a SnO\textsubscript{2} thin-film in the presence of NH\textsubscript{3}, N\textsubscript{2}, and H\textsubscript{2} is not a viable method in producing ZnSnN\textsubscript{2} thin-films. The thermodynamic kinetics of SnO\textsubscript{2} to ZnSnN\textsubscript{2} is simply unfavorable given the reactant gases and conditions laid out. The data elucidated four limiting factors to the production of ZnSnN\textsubscript{2}. They are as follow

1. **At 550°C NH\textsubscript{3} reactivity is too low for either solid state conversion or reduction of SnO\textsubscript{2}**

   While ZnSnN\textsubscript{2} formation could theoretically occur at 550°C, the availability of an activated nitrogen species from NH\textsubscript{3} is simply too low, and thusly SnO\textsubscript{2} remains in its stable solid form.

2. **The rate of SnO\textsubscript{2} reduction at 550°C in the presence of H\textsubscript{2} occurs at a much higher rate than Zn/Sn nitride formation**

   Theoretical equilibrium calculations showed that the reduction of SnO\textsubscript{2} by H\textsubscript{2} can be done with very low H\textsubscript{2} ambient pressures. The empirically derived data corroborated this result by showing that SnO\textsubscript{2} did in fact reduce to liquid Sn in the presence of H\textsubscript{2} compositions <7%.

3. **At 600°C NH\textsubscript{3} reactivity is high enough to lead to full scale SnO\textsubscript{2} reduction**

   It has been noted that NH\textsubscript{3} cracking efficiency is in part a function of temperature, with peak efficiency occurring around 600°C. Under the conditions provided however, nitrogen at 600°C seems to be providing an H\textsubscript{2} pressure in excess of ambient H\textsubscript{2}O, leading to the complete reduction of SnO\textsubscript{2} to liquid Sn.
4. **SnO$_2$ thin-films are stable at 600°C in the presence of an inert gas**

Equilibrium thermodynamics also showed SnO$_2$ to be stable at 600°C. In the end, some reduction was seen; however given the equilibrium constant for the reduction of SnO$_2$ in the presence of H$_2$, this small amount of reduction is likely caused by H$_2$ contamination rather than thermal decomposition.
The Gibbs free energy is a function of temperature for each reaction species. G(T) is derived from experimental data obtained through calorimetric measurements at constant pressure $P^o$ [Chase1998]. For the Gibbs free energy, $P$ is taken as $P^o=1\text{atm}$. The empirically derived data is then fitted with a cubic function to give Gibbs free energy as a function of temperature. The fitting coefficients are listed in table A.1 for a function of the form

$$G^o(T) = A + BT + CT^2 + DT^3$$  \hspace{1cm} (A.1)

<table>
<thead>
<tr>
<th>Compound</th>
<th>A(J)</th>
<th>B(J/K)</th>
<th>$B(J/K^2)$</th>
<th>$D(J/K^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$</td>
<td>-584,921.94</td>
<td>-15.739</td>
<td>.07663</td>
<td>$1.104 \times 10^{-5}$</td>
</tr>
<tr>
<td>SnO (Gas)</td>
<td>-19,908</td>
<td>-217.46</td>
<td>-.03621</td>
<td>$5.438 \times 10^{-6}$</td>
</tr>
<tr>
<td>SnO (Solid)</td>
<td>-290,799</td>
<td>-19.84</td>
<td>-.07441</td>
<td>$1.553 \times 10^{-6}$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>-1078.34</td>
<td>-191.29</td>
<td>-.03317</td>
<td>$4.772 \times 10^{-6}$</td>
</tr>
<tr>
<td>H$_2$O (Gas)</td>
<td>-242,939.7</td>
<td>-173.76</td>
<td>-.0365</td>
<td>$4.7547 \times 10^{-6}$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>-59,000</td>
<td>125</td>
<td>-48.8</td>
<td>$-9 \times 10^{-6}$</td>
</tr>
<tr>
<td>Zn (Liquid)</td>
<td>4277.05</td>
<td>-32.322</td>
<td>-.03777</td>
<td>$6.978 \times 10^{-6}$</td>
</tr>
<tr>
<td>Zn (Gas)</td>
<td>129,194.63</td>
<td>-149.33</td>
<td>-.02585</td>
<td>$4.893 \times 10^{-6}$</td>
</tr>
<tr>
<td>Sn (Liquid)</td>
<td>7995.72</td>
<td>-57.498</td>
<td>-.02726</td>
<td>$4.102 \times 10^{-6}$</td>
</tr>
<tr>
<td>H$_2$</td>
<td>-13,000</td>
<td>180</td>
<td>-48.8</td>
<td>.0275</td>
</tr>
</tbody>
</table>

Table A.1: A list of fitting parameters for $G^o(T)$ of the form Eq. A.1 using empirically derived calorimetric data. The function is fitted to temperature ranges from 298K-1600K.

The above parameters and the subsequent $G^o(T)$ for the different compounds are plotted below in figure A.1.
Figure A.1: A plot of $G'(T)$ for the species listed in table A.1 after being fitted to the cubic fitting function described by Eq. A.1.
B.1: Reynolds Number and Reactor Flow Characterization

The Reynolds number, a dimensionless quantity, is used to describe the flow characteristics of a fluid. The value of the Reynolds number for a given system can be used to indicate the nature of the flow profile, i.e. if the flow is either laminar (smooth) or turbulent in nature. Given the nature of the growth apparatus and the experiments, it is important to insure that the flow of reactant gases exhibit consistent laminar flow characteristics. As such, the Reynolds number, $R_e$, for the growth chamber can be characterized as a gas moving within a cylindrical pipe, and is described below by equation B.1 [Johnson1998].

$$R_e = \frac{\rho v_s L}{\eta}$$  \hspace{1cm} (B.1)

Where $\rho$ is the gas density in kg/m$^3$, $v_s$ is the mean velocity of the gas in m/s, and $\eta$ is viscosity in Pa-s. Since the gas composition of the system is made up of a multitude of gases, the total viscosity of the system has to take into account the combined effects of each gas represented in the mixture. For a single compound fluid, the viscosity as a function of temperature is described by Sutherland’s formula, which is written as

$$\eta(T) = \eta_o \left( \frac{T_o + C_s}{T + C_s} \right) \left( \frac{T}{T_o} \right)^\frac{3}{2}$$  \hspace{1cm} (B.2)

Where $C_s$, $T_o$, and $\eta_o$ are constant described in table B.1 and taken from [Weast1975].

The values of B.1 only include $N_2$, $H_2$, and $NH_3$. The reason for this is that the Sutherland constants for Zn vapor are poorly characterized. It can, however, be safely presumed that the change in viscosity from the introduction of Zn is negligible given the exceedingly small percent composition of Zn vapor in the reactant gas mixture.
Appendix B | Reynolds Number and Reactor Flow Calculations

<table>
<thead>
<tr>
<th>Reactant Gases</th>
<th>$T_o(K)$</th>
<th>$C_o(K)$</th>
<th>$\eta_o (10^{-6} \text{ Pa s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>300.55</td>
<td>111</td>
<td>17.81</td>
</tr>
<tr>
<td>$H_2$</td>
<td>293.85</td>
<td>72</td>
<td>8.76</td>
</tr>
<tr>
<td>$NH_3$</td>
<td>293.15</td>
<td>370</td>
<td>9.82</td>
</tr>
</tbody>
</table>

Table B.1: Table of values for Sutherland’s constant at the measured temperature $T_o$.

This method however calculates only the viscosity for a homogeneous single compound fluid. To calculate the viscosity of a multi fluid system requires the use of the Refutas equation, in which a viscosity blending number (VBN) is given for each species [Maples2000]. This equation is written as

$$VBN_i = 14.534 \times \ln[\ln(\eta_i + 0.8)] + 10.975$$

(B.3)

The total VBN is then the sum of VBNs times the percent composition of each species in the mixture,

$$VBN_{mixture} = \sum_i x_i \times VBN_i$$

(B.4)

This total VBN can then be used to estimate the viscosity by using the Refutas equation which is written as

$$\eta_{mixture} = \Re\left\{\exp\left(\exp\left(\frac{VBN_{mixture} - 10.975}{14.534}\right)\right) - 0.8\right\}$$

(B.5)

The values for $VBN_{mixture}$ and $\eta_{mixture}$ for growths 1-3 are tabulated below in table B.2.

To calculate the Reynolds number it is also necessary to calculate the total density of the gas. To do this we first need to calculate the density per species present, which can be derived as a function of pressure and temperature and written as

$$\rho_i = \frac{m_i P}{RT}$$

(B.6)

where $m_i$ is the molar mass in g/mol, and $R$ is the gas constant in J/K. One can find the total density by multiplying the partial volume fraction $x_i(V)$ of each species by the density and summing over all species.
Appendix B | Reynolds Number and Reactor Flow Calculations

\[
\rho_{\text{mixture}} = \sum_i x_i(V)\rho_i(T) \tag{B.7}
\]

The final aspect required in calculating the Reynolds number is the mean velocity, which is given by the flow through the pipe. This can be expressed as

\[
v_s = \frac{Z}{A} \tag{B.8}
\]

Where \( Z = 1.6 \times 10^{-4} \text{ m min/cm/s} \) is a constant required for the unit conversion between SCCM and m/s, while \( f \) is the total flow of the gas in SCCM and \( A \) is the cross sectional area of the reactor tube. The tube is 30mm in diameter making \( A=7.06 \text{ cm}^2 \). Taking these factors into account, it is possible to tabulate the Reynolds number for each experiment, with a pressure of 715.5 Torr for all four growths, and an overall tube length of .5 meters. These values are listed in table B.2.

<table>
<thead>
<tr>
<th>Growth</th>
<th>Temperature (K)</th>
<th>( \frac{H_2/N_2/NH_3}{(%)} )</th>
<th>( \eta_{\text{mixture}} ) (Pa s)</th>
<th>( \rho_{\text{mixture}} ) (kg/m³)</th>
<th>( f\text{(SCCM)} )</th>
<th>( R_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>823</td>
<td>0/25/75</td>
<td>2.81 \times 10^{-5}</td>
<td>.23</td>
<td>60</td>
<td>5.56</td>
</tr>
<tr>
<td>2</td>
<td>823</td>
<td>07/0/93</td>
<td>2.51 \times 10^{-5}</td>
<td>.22</td>
<td>75</td>
<td>7.44</td>
</tr>
<tr>
<td>3</td>
<td>873</td>
<td>0/25/75</td>
<td>2.94 \times 10^{-5}</td>
<td>.21</td>
<td>60</td>
<td>4.86</td>
</tr>
<tr>
<td>4</td>
<td>873</td>
<td>0/1/0</td>
<td>3.68 \times 10^{-5}</td>
<td>.18</td>
<td>60</td>
<td>3.32</td>
</tr>
</tbody>
</table>

Table B.2 Values for viscosity and \( R_e \) as a function of temperature and percent composition of reaction species.

A Reynolds number \(<10\) indicates a flow which exhibits laminar characteristics. For a pipe, a turbulent flow would have a \( R_e>2000 \), therefore given the above estimations, the reactor under the given growth conditions can be considered laminar.

**B.2 Zn Flow Rate Calculations**

Zn flow rate can be calculated as a function of vapor pressure, as well as the geometry of the opening of the Zn crucible. The theoretical calculations for Zn evaporation rate in g/min can be described as follows
where $\alpha$ is a proportionality constant equal to $0.003559 \frac{g}{min atm mm^2}$, $A$ is the area of the crucible opening, and $P_{eq}(T)$ is the temperature dependent equilibrium vapor pressure of Zn. The equilibrium vapor pressure is derived from empirical data. The fitting function and parameters were derived by Klimova et al. and the equation is detailed below with error included [Klimova2005].

$$\log_{10}(P_{eq}(T)) = \frac{-6224 \pm 187}{T} + 8.096 \pm 0.89$$

Equation B.8 is in g/min, with $T$ in kelvin, however since the flow rate is more useful in cm$^3$/min (SCCM), a factor of 342.6 cm$^3$/g has to be multiplied to $\kappa_{evap}(T)$ to make the unit conversion. A factor of .7 is also included in the calculation of flow to indicate losses of Zn due to backflow and condensation, which leaves an estimated 70% Zn to impinge on the substrate surface. The plot of $\kappa_{evap}(T)$ including losses presented in figure B.1 below.

![Figure B.1: A plot showing the temperature dependence of Zn flow rate $\kappa$ in SCCM. This theoretical estimation is considered an upper limit for Zn vapor pressure. Actual estimations data for Zn flow rate for the four experiments are tabulated below in table B.3.](image-url)
Table B.3: The above shows the actual vs theoretical flow rates for growths 1-4. The larger theoretical values of flow rate have been attributed to the formation of ZnO on the melt. This is corroborated by the fact that flow decreased in environments without H\textsubscript{2}, and increased in the presence of NH\textsubscript{3} at 600°C.

### B.3 Reactor Pressure Drop Calculations

While it is impossible to know the exact pressure everywhere in the reactor, based on the previous Reynolds number calculations, it is safe to assume for the reactor used that pressure is approximately constant everywhere and is equal to the measured pressure at the manometer. To confirm this, it is taken as an exercise to measure the pressure drop across the reactor vessel, insuring that the design implemented allows for experimental conditions to be consistently met.

Following the methodology outlined in [Pesheh2008], and [Kittel2002], we can derive an equation that expresses the force caused by the pressure differential in a tube of length \( L \) and cross-sectional area \( A \). This force is caused by the momentum transfer of particle collisions with the tube. We begin with a momentum transfer of \( M_a \nu_s \), and a collision rate of

\[
\bar{r} = \frac{1}{4} \pi L d n \bar{u} \quad (B.10)
\]

where \( M_a \) is the atomic mass of an individual species, \( \nu_s \) is the flow velocity, \( n \) is the number of moles of gas, and \( \bar{u} \) is the Maxwellian velocity distribution of the gas. With this in mind, it is possible to then derive the differential pressure as

\[
\Delta P = \frac{\bar{r} \rho}{A} = \frac{L}{d} n \bar{u} M \nu_s \quad (B.11)
\]
Appendix B | Reynolds Number and Reactor Flow Calculations

Since our gas is not homogeneous, but rather a mixture, it is required that we consider the sum of contributions of each gas. This, however, assumes that the mixture is ideal and non-interacting between species. With that in mind, the total pressure differential is simply the sum of forces for each species times the flow velocity and $L/d$, the length and diameter of the tube respectively.

$$\Delta P = \frac{L\nu}{d} \sum_i n_i \bar{u}_i M_i$$ (B.12)

Where we have rewritten $n$, $\bar{u}$, and $M$ in terms of species $i$. The Maxwellian distribution of velocity is equal to

$$\bar{u}_i = \sqrt{\frac{8k_BT}{\pi M_i}}$$ (B.13)

To calculate the total pressure, it is also necessary to calculate the number of moles of each species. Using the ideal gas law, it is possible to rewrite $n_i$ in terms of the partial pressure of the species

$$n_i = \frac{x_i PV}{RT}$$ (B.14)

where $x_i$ is the mole fraction of the reactant species. Including $v_i$ in terms of flowrate $f$, we arrive at the final form of $\Delta P$.

$$\Delta P = \frac{2fP_l^2}{dRT} \sum_i x_i \bar{u}_i M_i$$ (B.15)

The pressure drop for the varying growths conducted are tabulated in table B.4 for a tube diameter of $d=30$ mm, and $L=500$ mm, at $P=715.5$ Torr.

<table>
<thead>
<tr>
<th>Growth</th>
<th>Temperature (K)</th>
<th>$H_2/N_2/NH_3$ (%</th>
<th>$f$ (SCCM)</th>
<th>$\Delta P$ (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>823</td>
<td>0/25/75</td>
<td>60</td>
<td>.0027</td>
</tr>
<tr>
<td>2</td>
<td>823</td>
<td>07/0/93</td>
<td>75</td>
<td>.0037</td>
</tr>
<tr>
<td>3</td>
<td>873</td>
<td>0/25/75</td>
<td>60</td>
<td>.0260</td>
</tr>
<tr>
<td>4</td>
<td>873</td>
<td>0/1/0</td>
<td>60</td>
<td>.0241</td>
</tr>
</tbody>
</table>

Table B.4: values for estimated pressure drop $\Delta P$ for each of the four growths based on percent composition, temperature, and flow rate of the reactant species.
The results show that the drop in pressure within the reactor is small in comparison to the overall pressure, as well as the overall uncertainty in pressure, thusly indicating that under the conditions studied, gas pressure within the reactor can be assumed constant.
C.1 X-ray Diffraction Setup and Instrument Characterization

The main characterization tool used in the aforementioned research was powder X-ray diffraction done on a Scintag® X-1 X-ray diffractometer. Given a thin-film thickness of or less than ~1.5μm in thickness, a theta scan grazing-incidence geometry was used in order to maximize measurements of the thin-films as opposed to the background from the thicker underlying amorphous substrate. To do this, the X-ray source was fixed at an angle Ω with respect to the surface of the specimen, while the detector was moved by θ. This setup allowed for high signal to noise by reducing the amount of incidence on the underlying glass. A schematic of the aforementioned diffractometer geometry is illustrated below in Figure C.1.

Figure C.1: A depiction of the fixed grazing-incident diffractometer geometry and location of relevant hardware.
The values of the divergence, receiving, and scatter slit widths (mm) for the X-ray source and detector are listed below in table C.1.

<table>
<thead>
<tr>
<th></th>
<th>Divergent (mm)</th>
<th>Scatter (mm)</th>
<th>Receiving (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray source</td>
<td>1.0</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>Detector</td>
<td>-</td>
<td>0.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table C.1: A list of relevant slit parameters for measurements taken of growths 1-4.

The X-ray tube was a Cu target with Kα characteristic X-rays at a wavelength of $\lambda=1.5403$ Å. Calibration was done prior to every set of measurements, insuring correct theta, omega, and substrate angle orientations. To check alignment, an Al$_2$O$_3$ NIST test target (SRM1976b) was used [Kaiser2008]. The target was made of sintered alumina powder with an average grain size of $\sim$3μm. The target was used to check for instrumental peak shifting as well as to measure the inherent instrumental line broadening of the device. Figure C.2 shows the XRD diffraction pattern and the measurement of the characteristic instrumental line broadening using the $I/I_0=100$ peak at $2\theta=35.17^\circ$.

![Image of XRD data](image_url)

Figure C.2: plot a.) shows the grazing incidence spectra for the Al$_2$O$_3$ 1976b calibration standard for 20’s of 20° to 60°. b.) depicts the $2\theta=35.17^\circ$ peak fitted with a 7th order Gaussian fit indicating an instrumental broadening of $\Delta(2\theta)=.0038$Rad. These measurements were taken with a step size of .04° and integration time of 2 seconds.
C.2 Average Grain Size Measurements

It is possible to calculate the size of different grain orientations directly from X-ray powder diffraction data. There are several methods, including Reitveld analysis, which can be used to find average grain size, however the most straightforward and common formalism is the Scherrer equation, which is written below.

\[
\tau = \frac{0.9 \lambda}{\beta \cos(\theta)}
\]  

(C.1)

For Eq. C.1 \( \lambda \) is the characteristic X-ray wavelength in meters, \( \beta \) is \( \Delta(2\theta) \) for the peak in question minus the characteristic instrumental line width and measured in radians, and \( \theta \) is the Bragg scattering angle. The factor of .9 is a dimensionless quantity known as the shape factor, and often denoted as \( K \), which is \( \sim .9 \) for most substances. To calculate \( \beta \) for the material in question, the FWHM for the peak in question must first be calculated. DeGraef and others suggest Lorentzian or Gaussian fitting as the most precise way for calculating this value [DeGraef2007]. The form of the analytic Gaussian function for a peak of height \( I_o \) and width \( w \) is given as

\[
I_{gaussian}(x) = I_o \exp \left( \ln \left[ 2 \left( \frac{a-2\theta}{w} \right)^2 \right] \right)
\]  

(C.2)

This however presumes a perfectly symmetric Gaussian with peak width \( w=\Delta(2\theta) \), sometimes just denoted as \( w \), however due to inherent asymmetries in the actual peaks, a more precise method involving the use of high order Gaussian fitting was done, with the numerical calculation of \( \Delta(2\theta) \) made from the resulting fit. This is done by taking the sum of Gaussian functions as follow,

\[
I_{fit}(x) = \Sigma_i a_i \exp \left( 2 \left( \frac{x-b_i}{c_i} \right)^2 \right)
\]  

(C.3)
where $a$, $b$, and $c$ are fitting parameters. Using this, an equation with $3i$ parameters can be created. It was found that $R^2$ for the fit converged at $i=6$-$7$, with values of $R^2 \sim .99$ for all fits. With this function, it is then possible to numerically solve for the $\Delta(2\theta)$ for the peak in question. With $\Delta(2\theta)$ numerically calculated, as well as the characteristic line-broadening of the X-ray diffractometer, it is now possible to solve for $\beta$ in radians

$$\beta = \Delta(2\theta)_{\text{peak}} - \Delta(2\theta)_{\text{instrument}}$$

(C.4)

where $\Delta(2\theta)_{\text{instrument}}$ is simply the instrument’s characteristic line width, which is derived as the line width of the characteristic $2\theta=35.17^\circ$ of the $\text{Al}_2\text{O}_3$ test standard. This value can be used since the average grain size of the $\text{Al}_2\text{O}_3$ sample is much larger than $\sim .2 \mu$m, which is the limit for the Scherrer equation’s predictive capabilities, and where instrumental broadening becomes the dominant effect. With this in place, it is now possible to calculate the average grain size of the various orientations. To illustrate, table C.2 contains relevant fitting and grain size estimations for the characteristic [121] $\text{SnO}_2$ plane for unconverted $\text{SnO}_2$, and reacted films from growths 1 and 4, which showed relatively intact $\text{SnO}_2$ films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta$ (°)</th>
<th>$\Delta(2\theta)$ (Rad)</th>
<th>$\tau$ (1E-9m)</th>
<th>$i$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreacted SnO₂</td>
<td>51.76°</td>
<td>.0063</td>
<td>60.8</td>
<td>6</td>
<td>.99993</td>
</tr>
<tr>
<td>Growth 1</td>
<td>51.74°</td>
<td>.0058</td>
<td>76.94</td>
<td>6</td>
<td>.99991</td>
</tr>
<tr>
<td>Growth 4</td>
<td>51.7°</td>
<td>.0057</td>
<td>79.98</td>
<td>6</td>
<td>.99992</td>
</tr>
</tbody>
</table>

Table C.2: Shows values of Bragg angle $\theta$, peak width $\Delta(2\theta)$, and average grain size, $\tau$, along with $R^2$, the deviation of the fit from the data to that of the data’s mean deviation.

Figure C.2 shows the data and fitting used for the Scherrer calculations in table C.2. This data, however, must be carefully considered, as it is an incomplete picture of line-broadening mechanisms. Other factors, such as non-uniform strain play a part in the final grain size calculation. The data however is consistent with data obtained by Patil et al. and Kose et al.
concerning the increase in grain size with annealing temperature and time of SnO$_2$ thin-films, as well as the inclusion of uniform strain, which manifest itself as a shift in $2\theta$ peak location [Patil2011, Kose2014]. While non-uniform strain cannot be ruled out as a possible source of line-broadening, it can be seen as minimal in effect. The substrate had upwards of 12 hours to cool after each growth, allowing for non-uniform strain to be released slowly before dropping below the strain point. Nonetheless, the estimated average grain size should be considered the lower bounds of the actual grain size.

Figure C.3: Depicts the effect that various growth conditions have on the characteristic [121] line. Line broadening or narrowing indicates changes in the average grain size or the introduction of non-uniform strain, while a shift in the peak resonance indicates the introduction of uniform lattice strain.
Appendix D | Reactor Purging and Cleaning Procedure

Because of the damaging effects of H₂O and oxides on the growths, careful attention was paid to the preliminary purging and cleaning process of the reactor. The following outlines the steps used to effectively remove contaminant gases to that of operable levels:

1. Turn on rotary-vane pump and let warm up for 1-2min
2. Open butterfly valve, set to 240Torr with 500SCCM flow of N₂
3. Once pressure reaches 300Torr, set pressure to 10.5Torr
4. Once stabilized, pump down for ~1hour
5. Once pressure has equalized, close butterfly valve to isolate reactor chamber. Once closed, check pressure to indicate the maintenance of vacuum
6. If no loss of vacuum is detected, raise pressure to 715.5Torr
7. Once pressure is stabilized, repeat steps 2, 3, and 6 three more times
8. Open valves and flow gas through NH₃/H₂ for ~1hour to purge lines
9. Close NH₃/H₂ lines, set furnace temperature to 200°C at 10.5Torr and 500SCCM of N₂, letting the reactor “bakeout” overnight.

Another important cleaning procedure is that of the tube itself. Zn vapor condenses on the tube surface, quickly forming the stable ZnO. To reduce any ill effects, the Zn/ZnO is cleaned off the tube via a 1:4 68% nitric acid/DI water solution. The tube is let to sit in the acid solution for 1 minute, followed by a thorough rinse with DI water. This process is repeated twice.


Bibliography


