SYNTHESIS AND CHARACTERIZATION OF ZINC TIN NITRIDE: A CHARGE-NEUTRAL ORDERING MODEL FOR WURTZITE-BASED HETEROVALENT TERNARY COMPOUNDS

by

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* We also certify that written approval has been obtained for any proprietary material contained therein.
To my Mom and Dad and brother Tom.
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PAUL C. QUAYLE

Abstract

The atomic positions of the Zn-IV-N$_2$s are nearly the same as those of the III-Ns. ZnSnN$_2$ is the low band gap member of the Zn-IV-N$_2$s with a direct gap of 1.7 eV. By studying the synthesis and characterization of ZnSnN$_2$, we reveal information on the Zn-Sn-N phase space that is important for future experiments on ZnSnN$_2$ and we uncover information related to cation disorder that applies to all wurtzite-based heterovalent ternary compounds.
In this thesis, we describe the synthesis of ZnSnN$_2$ by a vapor-liquid-solid technique employing a Zn-Sn melt and a nitrogen plasma. Samples of ZnSnN$_2$ are distinguished from Sn$_3$N$_4$ and Zn$_3$N$_2$ by Raman spectroscopy and by Auger chemical analysis. Sn$_3$N$_4$ precipitates from the melt at temperatures between 440 and 560 °C in the absence of Zn. Zn$_3$N$_2$ grows only in the vapor phase, at melt temperatures between 409 and 463 °C. ZnSnN$_2$ precipitates from the melt at melt temperatures between 455 and 560 °C, for melt compositions of 1.5 - 15 at. % Zn.

Disorder on the cation sublattice of wurtzite-based ABC$_2$ compounds is investigated under the constraint that the octet-rule be preserved. We show that, with the exception of a highly symmetric twinned structure, all possible orderings can be described as a mixture of the Pna2$_1$ and Pmc2$_1$ orthorhombic phases. We describe the system using a pseudospin model. The Raman, x-ray diffraction and photoluminescence spectra of ZnSnN$_2$ are interpreted in light of the ordering model presented here.

Finally, we investigate cation disorder in the wurtzite-based ABC$_2$ compounds with the octet-rule-preserving constraint relaxed. The role of cation exchange defects is explored in depth. We provide evidence of an energetic benefit to the clustering of exchange defects and we demonstrate that clusters of exchange defects are equivalent to units of the Pmc2$_1$ phase embedded within the ground-state Pna2$_1$ phase.
1. Introduction to the Zn-IV-nitrides:

ZnSnN$_2$ is the small band gap member of the Zn-IV-N$_2$ set of semiconductors, which are the ternary analogs to the binary III-nitride alloys. Interest in ZnSnN$_2$ has taken hold recently with 20 of its total 24 reports in the literature having been published since 2011. Paudel, Punya, van Schilfgaarde and Lambrecht first predicted the optical, crystalline and phonon properties ZnSnN$_2$ in the late 2000s and 2011 [1,2,3,4]. The first literature report of its synthesis in 2012 demonstrated that ZnSnN$_2$ can be synthesized in a stable form and measurement of its fundamental properties began [5,6,7]. ZnSnN$_2$ can be synthesized between room temperature and 553 °C in both stoichiometric and off-stoichiometric phases [8]. ZnSn$_x$Ge$_{1-x}$N$_2$ alloys have been grown with $x = 0.37$, 0.40, 0.51, and 0.71 [9,10]. This initial work has established the potential of ZnSnN$_2$ as a functional material for photovoltaic, optoelectronic and power electronic applications that is composed of nontoxic and abundant elements.

There is currently no consensus among researchers regarding the effect of cation disorder on the electronic band structure of ZnSnN$_2$. Results from photoluminescence measurements of highly disordered ZnSnN$_2$ indicate a direct band gap of 1.7 eV [11]. These results contrast with other band gap determinations that suggest a cation disorder induced tunable band gap in ZnSnN$_2$ [5,8,13-15]. The evidence as a whole indicates that a certain type of cation
disorder leaves the electronic structure of this semiconductor unchanged from the ideally ordered band gap, while another type of disorder decreases the band gap.

The atomic positions of the ternary nitrides are nearly the same as those of the binary nitrides. The wurtzite structure of the binary nitrides is pictured in Fig. 1, along with three ternary orthorhombic phases. In ZnSnN₂, the Pna₂₁ phase is calculated to be only 0.01 eV per formula unit (fu) more stable than the Pmc₂₁ phase [11]. Unlike the Pna₂₁ and Pmc₂₁ phases, which consist of tetrahedra of two group II and IV cations surrounding each group V anion, the Pm3₁ phase consists of tetrahedra of three group II cations and one group IV cation or vice versa surrounding each group V anion. Thus, unlike the two other phases, the Pm3₁ phase violates the octet rule and it has a significantly higher calculated energy of formation than the other two phases [11].
Figure 1.1. Projection of the binary wurtzite and ternary orthorhombic crystal structures on the \(c\) plane. Primitive cells are outlined.

Figure 2 shows that the ordered Zn-IV-N\(_2\) alloy band gaps span the visible spectrum from 1.7 to \(\sim 5.5\) eV. This alloy band gap situation is similar to that of the III-N alloy band gaps, which extend from the infrared to the deep ultraviolet [16]. In addition, the alloy band gaps of the technologically important ternary Cu(In,Ga)Se\(_2\) (CIGS) semiconductors extend from 1.0 to 1.7 eV [17,18]. Thus, the Zn-IV-N\(_2\) alloys are
another semiconductor system that spans an interesting region of the light spectrum. In addition, these ternaries are predicted to have rich defect and doping characteristics, as well as low differences in spontaneous polarizations relative to each other [19].

Figure 1.2 (taken from Ref. 7). The band gaps versus “a” lattice constants for III-nitrides and Zn-IV-nitrides and their alloys. Here, for appropriate comparison, the orthorhombic “a” lattice constants of Zn-IV-nitrides are divided by factor 2. Experimentally determined values for pure materials are shown by solid circles. III–V lattice constants, band gaps, and bowing parameters are from Ref. 20 and references therein. The experimentally determined band gap of ZnGeN₂ is taken from Ref. 21, that of ZnSiN₂ is taken from Ref. 22, and that of ZnSnN₂ is from this work. Calculated values are shown by open circles [4]. ZnSiN₂ is predicted to be indirect gap; here both the indirect gap and the gap at Γ point are shown. The alloys ZnSi₁₋ₓ(Ge,Sn)ₓN₂ are predicted to be direct up to about x=0.6–0.7, or to a band gap of 4.5–4.6 eV, using interpolations of the band structures from Ref. 4. The bowing parameters for Zn–IV-nitrides are taken to be proportional to the differences in ternary band gaps, with the constant of proportionality set equal to that found for III-nitrides [20].
ZnSnN$_2$ is a member of the broad set of heterovalent ternary semiconductors [23,24]. Goryunova and Parthe (1967) outlined the extent of this set by determining all possible stoichiometries for both normal ternary compounds and more complex ternary compounds that have polyanionic and polycationic arrangements that include multiple anion-anion and cation-cation bonds [25].

The II-IV-V$_2$s are normal valence compounds that obey a simplified general equation since $2x$ (group II valence electrons) + $2x$ (group IV valence electrons) = $4x$ ($8$ – group V valence electrons). In other words, the octet rule is fulfilled.

Of course, not every theoretical compound can be formed. Accordingly, the results are refined by experimental observations to give a small number of ‘guidelines’ as to which compounds are stable. Two of these guidelines are 1) a simple formula and small number of atoms per formula unit are preferred, and 2) the stability of ternary compounds varies with the stability of the binary ‘base’ structures (for example, the base structures of ZnSnN$_2$ are Sn$_3$N$_4$ and Zn$_3$N$_2$). The results and predictions of Goryunova and Parthe for II-IV-V$_2$ compounds are reproduced in Table 1.
Table 1.1. The formation of II-IV-V$_2$ compounds (taken from Goryunova and Parthe [25]). Group II atoms are listed in the leftmost column, group V in the topmost row and group IV in the row underneath.

<table>
<thead>
<tr>
<th>Nitrides</th>
<th>Phosphides</th>
<th>Arsenides</th>
<th>Antimonides</th>
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<tr>
<td>Be</td>
<td>+</td>
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<td>?</td>
</tr>
<tr>
<td>Mg</td>
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<td>Zn</td>
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<td>Ra</td>
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</table>

- Existence of a compound is hardly probable
- A compound exists and can be predicted
- Compound is predicted with high degree of probability
- Compound is predicted, but an analysis in greater detail is necessary
- No information on binary system

Shortly after Table 1 was published there was a small boom in ternary nitride growth. ZnGeN$_2$ was first grown in 1970 by Maunaye, Lang and colleagues [26,27], and shortly after in 1974 by Larson, Maruska and Stevenson [28]. The nitrides MgSiN$_2$, MgGeN$_2$ [29], CaGeN$_2$ [30], BeSiN$_2$ [31], BaSiN$_2$ [32,33], CaSiN$_2$ and SrSiN$_2$ [34] were also studied in the 1960s and early 1970s. These early growths did not however begin a period of intense research into the nitrides, and ZnSiN$_2$ was not grown until 1992 [35]. On the other hand, the chalcopyrites, especially ZnGeP$_2$, CdGeAs$_2$ and AgGaSe$_2$, received a tremendous amount of interest because of their birefringent properties, which positioned them for nonlinear optics applications. The ternary nitrides had no such clear application and interest lagged as the quality of n-type and p-type GaN and InGaN progressed to device levels [36,37].
Evidence of this situation is seen in a 1994 U.S. Army Research Office technical report on bipolar transistors composed of heterojunctions of GaN and InGaN or ZnGeN$_2$. The report concludes, “Because our results with In$_x$Ga$_{1-x}$N have been so promising, we did not pursue the deposition of ZnGeN$_2$” [38].

ZnSnN$_2$ was not grown until 42 years after ZnGeN$_2$ and 20 years after ZnSiN$_2$. In this case, there is a clear physical reason for the delay; ZnSnN$_2$ is less stable than ZnGeN$_2$ and ZnSiN$_2$ [19]. ZnSnN$_2$ has not yet been synthesized at temperatures greater than 553 °C. This apparent ceiling in the growth temperature prevents synthesis using the standard nitrogen source of ammonia, which requires a temperature greater than 550 °C to become activated [34,39]. As a result, the use of a nitrogen plasma has become the standard for ZnSnN$_2$ synthesis. Since its first report in the literature, grown by plasma-assisted molecular beam epitaxy in 2012 [5], ZnSnN$_2$ has been grown by three different plasma-assisted methods: RF sputtering [6], vapor-liquid-solid [7], and DC magnetron sputtering [12].

The remainder of this chapter outlines the rest of the thesis. Chapter 2 begins with additional background on the growth of ZnSnN$_2$, followed by a description of the VLS method used for the synthesis of ZnSnN$_2$, Zn$_3$N$_2$ and Sn$_3$N$_4$ described in this thesis and the methods used to identify these materials. Closing the chapter will be a discussion of contributions from this work to the issue of the energetic stability of ZnSnN$_2$ based on the material yielded as a function of parameter space.
In Chapter 3 we characterize the ZnSnN$_2$ sample grown by the VLS method at 485 0C. The lattice parameters measured by x-ray diffraction (XRD) spectroscopy are in good agreement with theory and with other measurements [5,6,7,11,19]. The XRD spectrum shows no signal of the superstructure peaks that distinguish the orthorhombic spectra from the wurtzite spectrum. This binary-like XRD spectrum is observed in all other measurements of ZnSnN$_2$ and is commonly seen in ternary compounds [24]; it is the result of a loss of order on the lattice due to cation disorder. Measurement of the band gap of ZnSnN$_2$ by photoluminescence (PL) and photoluminescence excitation spectroscopy (PLE) give a direct gap close to prediction [4,7,11].

In addition, we revisit the Raman spectrum of ZnSnN$_2$, which gives further evidence of cation disorder. The spectrum resembles the phonon density of states (DOS) and shows no indication of first-order vibrational modes. This amorphous-like Raman spectrum indicates a dramatic decrease in lattice periodicity.

It follows from the data of Chapter 3 that disorder on the ZnSnN$_2$ cation sublattices has a minimal effect on the band gap of the material. Measurement of the band gap by PL and PLE of material that looks amorphous in Raman spectroscopy gives a gap in close agreement with accurately predictive band structure calculations for perfectly ordered Pna2$_1$ crystals. These results are however at odds with calculations based on the random distribution of cations that predict a decrease of 1 eV for fully disordered material [40].
In Chapter 4 we address how to reconcile these seemingly contradictory observations. We propose that the lattice disorder in our ZnSnN$_2$ evident in the XRD and Raman spectra does not result from the random placement of cations on the group III sublattice, but from a more constrained type of disorder that preserves local charge neutrality, according to the octet rule. We investigate the possible orderings of cations with the restriction that the octet rule must be obeyed. We demonstrate that all possible orderings within this constraint can be viewed as combinations of the row stackings of the common basal plane occurring in Pna2$_1$ and Pmc2$_1$.

Finally, we explore the nature of disorder in ZnSnN$_2$ when the octet rule constraint is relaxed. Cation exchange defects have been shown to be particularly low in formation energy in the zincblende-based ternaries. Based on these results, we catalog the various types of cation exchange defects that can occur on the Pna2$_1$ lattice. These results demonstrate that a mixing of the Pna2$_1$ and Pmc2$_1$ phases can be due to the clustering of cation exchange defects.

We conclude the thesis with a summary and outlook for future work.
References


2. Synthesis of ZnSnN$_2$, Zn$_3$N$_2$ and Sn$_3$N$_4$

2.1 Background

Any effort to grow ZnSnN$_2$ has to address two main complications: the volatility of Zn and the presumed low dissociation temperature of ZnSnN$_2$. These complications preclude the use of ammonia as a nitrogen source at typical vapor growth pressures.

The volatility of Zn is so high that, in our VLS growth experiments, which have a crucible of molten Zn and Sn as the cation sources, the Zn is superheated above its boiling point. At 500 °C the vapor pressure of Zn is 460 mTorr; thus, for a melt with 25 % Zn, the vapor pressure of Zn is approximately 115 mTorr, which is four times the ambient growth pressure. Boiling, however, does not occur at this temperature due to the high surface tension of the melt [1,2]. For Sn, at 500 °C, the vapor pressure is eleven orders of magnitude lower than that of Zn.

A nitrogen plasma is widely used in the low temperature deposition of materials such as Si$_3$N$_4$ [3], C$_3$N$_4$ [4], GaN [5] and InN [6]. A radio frequency (RF) generated N$_2$ plasma contains N$_2$, atomic N and activated molecular nitrogen (N$_2^*$) species at pressure-dependent densities. N$_2^*$ is quenched by collisions; however, the loss of N by recombination into N$_2$ requires three-body collisions, which can be neglected at pressures in the mTorr range [7,8]. As a result, the N$_2^*$ density peaks at around 50 mTorr and is exhausted by 100 mTorr, and the N partial pressure increases
linearly well into the torr range. For GaN synthesis, the use of the N$_2^*$ species as the nitrogen source rather than atomic N results in faster growth rates and higher quality material, at least for GaN grown by MBE. This result is attributed to the lower activity of N$_2^*$ compared to atomic N. The latter, highly reactive species has been observed to ‘attack’ the surface of GaN [9].

Feldberg, Durbin and colleagues first reported the synthesis of ZnSnN$_2$ by MBE [10]. They dealt with the high vapor pressure of Zn by growing at a Zn:Sn flux ratio of 10:1, with Zn and Sn source temperatures of $\sim$ 275 and $\sim$ 1100 °C, respectively. Nonetheless, their material was Sn-rich with a Zn:Sn stoichiometry of 1:1.2. Synthesis with lower cation flux ratios resulted in Sn droplet formation.

Soon after the initial MBE work, Lahourcade, Atwater and colleagues reported the growth of ZnSnN$_2$ by RF magnetron sputtering [11]. Growth was done on both c sapphire and c plane GaN at 250 °C using a Zn$_{0.75}$Sn$_{0.25}$ target. Their material was identified as stoichiometric ZnSnN$_2$ based on chemical analysis by EDS and XRD structural analysis. The same group also synthesized the alloys ZnSn$_x$Ge$_{1-x}$N$_2$, with x = 0.71, 0.51, 0.40 and 0.37 [12].

Deng, Liu and colleagues grew ZnSnN$_2$ by DC magnetron sputtering using a Zn$_{0.75}$Sn$_{0.25}$ target [13]. Synthesis was done at room temperature and two samples were annealed at 300 and 400 °C in N$_2$ for 3 hours. Successfully synthesizing ZnSnN$_2$ at room temperature was an important development since it allows for the
deposition on low temperature flexible substrates like polyethylene terephthalate, as reported in Ref. 13.

Fioretti et al. used a combinatorial RF sputtering technique to grow Zn$_{1-x}$Sn$_x$N under many different conditions [15]. This growth technique uses temperature and Zn:Sn composition gradients applied to individual glass substrates to explore a wide range of parameter space, from 0.3 – 0.75 at. % Zn/(Zn+Sn) and 60 to 340 $^\circ$C. They also grew a sample at an isothermal value of 35 $^\circ$C using 0.3 – 0.75 at. % Zn/(Zn+Sn).

### 2.2 ZnSnN$_2$ growth by the vapor-liquid-solid method

#### 2.2.1 Experimental details

The vapor-liquid-solid (VLS) method is a good choice for growing ZnSnN$_2$ because the alloy melt provides an ample source of metal at the growth interface despite the high rate of loss of Zn from the surface. The incident activated N$_2$ is directed to the Zn-Sn melt, contained in a boron nitride crucible, by a quartz tube and dissociates upon interacting with the liquid surface, providing atomic nitrogen to the liquid. By varying the starting composition of the melt and the growth temperature, conditions were found for which either Zn$_3$N$_2$ or Sn$_3$N$_4$ or ZnSnN$_2$ could be grown while avoiding the formation of the other two materials.
Synthesis was done in a stainless steel vacuum chamber with a base pressure of $10^{-7}$ torr. By measuring the spectroscopic emission of the plasma using an OceanOptics spectrometer, we determined that 30 mTorr is the optimal pressure for nitride growth in our system since it generates the highest density of $\text{N}_2^*$ [8]. Temperature was measured by a thermocouple embedded in the base of the crucible.

Zn and Sn (5N) were refined of their native oxides and alloyed inside a nitrogen-filled glove box with 1 ppm O$_2$ and H$_2$O. Both metals were refined before alloying by melting each in a separate graphite crucible at 450 °C, in order to separate the metal from the oxide; the less dense oxide tended to float to the surface leaving purified metal at the bottom to be removed after cooling. Additionally, the graphite appeared to dissociate the tin oxide, leaving a shiny, specular surface where the metal was in contact with the crucible. The refined metals were then alloyed at 450 °C for 1 hour and stirred periodically. The alloy, typically of about 1.7 grams mass, remained in an inert atmosphere until it was loaded into the growth chamber. Exposure to atmosphere was limited to less than 15 seconds, although oxidation was observed in this transient period and even within the glovebox. After loading into the growth chamber, the remaining residual oxides were further removed by hydrogen plasma cleaning.

All growths proceeded in a similar manner. The alloy charge underwent a final H$_2$ plasma cleaning stage, the temperature was increased to the target growth
temperature and the gas flows were adjusted to the growth conditions. The growth plasma consisted of 1:8 sccm H$_2$:N$_2$ at a forward power of either 240 or 60 W. Once the N was incorporated, the melt surface took on a slightly darker tint. In most cases, total growth times were approximately 1 hour, but typically the surface would become increasingly matte and dark until entirely opaque within the first 15 minutes. Sample thicknesses were between 50 and 500 nm.

Detailed descriptions of the metal alloy charge preparation, the melt cleaning and the growth procedures are provided in appendices A and B.

Identification of the material was done using several methods. Raman spectra were taken using a solid-state laser (2.33 eV). All measurements were performed in ambient atmosphere. Lasers were focused onto the sample to 1-2 um diameter at normal incidence by a 50x microscope objective. Neither the incident nor emitted radiation was polarization-resolved.

Energy-dispersive x-ray spectroscopy was done with a FEI Quanta 3D environmental scanning electron microscope at an accelerating voltage of 30 keV. Auger electron spectroscopy (AES) was performed with a PHI 680 microprobe equipped with a field-emission scanning electron microscope set to a beam current of 10 nA and accelerating voltage of 10 keV. Argon sputtering to clean the surface was done with a PHI 06-350 gun at an accelerating voltage of 1 keV prior to the AES measurement.
2.2.2  Modeling of zinc diffusion through the melt

Zinc evaporation from the surface of the melt generated a Zn composition gradient and subsequent diffusion from the bottom of the melt to the top. We used a one-dimensional Fick’s law diffusion equation to model this composition profile versus time. Zn evaporation rates were estimated using the Langmuir mass loss relation shown in equation (1). This relation equates the equilibrium rate of incidence of atoms on the melt surface, given by the temperature dependent vapor pressure, to the equilibrium rate of mass loss in vacuum by evaporation [16]:

\[
\frac{dm}{dt} = A \sqrt{\frac{M}{2\pi RT}} P
\]  

where \( m \) is the mass of the Zn component of the melt, \( A \) is the melt surface area, \( M \) is the atomic mass of Zn, \( P \) is the equilibrium vapor pressure, \( T \) is temperature and \( R \) is the universal gas constant.

Equation 1 describes evaporation into an ideal vacuum and at low pressures where the mean free path of the gaseous atoms in the ambient is not diffusion limited. According to the formulation of Pieterse and Focke [17], this equation is valid for Zn at 30 mTorr if the diffusion coefficient in the ambient is on the order of \( 10^2 \text{ cm}^2/\text{s} \) or greater. Using the Chapman-Enskog equation, we estimate a diffusion coefficient for Zn vapor in N\(_2\) at 30 mTorr on the order of \( 10^4 \text{ cm}^2/\text{s} \)
Zn vapor pressures above the Zn/Sn alloys were calculated using well-determined thermodynamic data [19]. The vapor pressure of Sn is a negligible $10^{-13}$ torr at 500 °C.

### 2.2.3 Characterization of phases

Raman spectroscopy provided a clear way of determining each phase. Figure 2.1(a-g) displays characteristic spectra resulting from VLS growth for each material. Experimental spectra for the binaries are available in the literature.

The Raman spectrum of VLS-grown Sn$_3$N$_4$ in Fig. 2.1(a) corresponds very well with that reported in the literature reproduced in Fig. 1(b) [20]. Five peaks for Sn$_3$N$_4$ at 150, 246, 419, 528, and 626 cm$^{-1}$ are also present in the data published in Ref. 20. In addition, our spectrum includes peaks at 130 cm$^{-1}$ and 700 cm$^{-1}$, as well as less prominent features at 458, 653 and 741 cm$^{-1}$.

The Zn$_3$N$_2$ spectrum in Fig. 2.1(c) consists of two peaks, centered at approximately 250 and 575 cm$^{-1}$. These peak locations are slightly shifted from, and broadened in comparison to, those of Ref. 21 shown in Fig. 2.1(d), centered at 257 and 565 cm$^{-1}$. The broadening may be in part due to degradation of the sample by the well-documented conversion of Zn$_3$N$_2$ to ZnO upon exposure to humid air. This conversion was clearly seen in our material by an AES sputter depth analysis,
which was oxygen-rich at the surface and nitrogen-rich in the interior of the sample.

![Raman Spectra](image)

Figure 2.1 Measured Raman spectra. All three materials were grown by the VLS method. The measured spectra of Sn₃N₄ (a) and Zn₃N₂ (c) correspond well with the literature, (b) and (d), respectively [20,21]. The measured spectrum of ZnSnN₂ (e) [22] is shown along with the calculated phonon density-of-states broadened (f) and raw (g) [23].

Finally, Fig. 2.1(e) shows a characteristic Raman spectrum measured for polycrystalline ZnSnN₂ [22], along with the phonon density of states (DOS), taken from the literature, Figs. 1(f and g) [23]. The measured Raman spectrum correlates
very well with the broadened phonon DOS spectrum. This correspondence indicates a breakdown in the wave vector selection rules that we attribute to a dramatic loss of periodicity on the cation sublattice.

Each identification is corroborated by AES chemical analysis. Zn$_3$N$_2$ samples showed no Sn signal above a noise level of \( \sim 1 \) at. %. Sn$_3$N$_4$ showed quantities of Zn between noise levels and 5.0 at. %.

Figure 2.2 shows three AES spectra for the ZnSnN$_2$ sample grown at 485 °C. The trough around 400 eV is due to the N signal. This signal overlaps with Sn, as shown in the inset. The green curve is due to Sn only and the red and blue curves show the presence of N.

The key result from the AES spectra is the near equal quantities of Zn and Sn, which are each close to 25 at. %. The high quantity of O and C are artifacts that result from post-growth contamination. AES is a surface measurement tool that is capable of probing between \( \sim 10 - 100 \) angstroms, and is sensitive to surface contamination from atmosphere. Sputtering is done in order to probe the sample below the surface contamination, but this is limited in its capabilities. Oxygen and, to a lesser extent, carbon are mobile on the surface and tend to flow back into the sputtered sample portion from the surrounding surface. Also, sputtering dissociates N leaving an erroneously low measured quantity. We refer to the
Raman, photoluminescence and XRD discussed in chapter 3 to support the conclusion that the material is stoichiometric ZnSnN$_2$.

![Figure 2.2. AES sample of ZnSnN$_2$ grown at 485 °C. Measurements were taken at three different spots shown by the red, blue and green spectra. The inset shows an expanded view of the energy range where the N and Sn peaks overlap. The green spectrum (highlighted by the light green line) contains Sn only. Experimental uncertainty is ~1 at. %, derived from baseline noise.]

2.2.4 Growth dynamics

Using the formulas described in section 2.2.2, we modeled a representative experiment in Fig. 2.3 to illustrate the cleaning and growth processes. This model demonstrates how both the surface and average composition change during the experiment and the impact of the suppression of Zn evaporation by the
introduction of N$_2$ to the plasma at the onset of growth.

![Figure 2.3](image)

Figure 2.3. Model of the Zn composition change throughout a representative experiment. Top, temperature as a function of time. The growth stage begins when N$_2$ is added to the plasma. Bottom, Zn composition at the surface and averaged throughout the alloy melt.

Before growth, the oxides were diminished by exposure of the Zn-Sn melt to a H$_2$ plasma at 250 °C for approximately 340 minutes, which was sufficient time to diminish the oxides while evaporating only a couple percent of Zn. Next, the H$_2$ flow rate was increased to 80 sccm and an N$_2$ flow at 40 sccm was initiated, and the temperature was rapidly increased to the growth temperature. This ramp stage evaporated a large quantity of Zn, which was visible as a dense discharge of Zn from the melt surface that reacted with the H$_2$ plasma and emitted a red-pink glow. Other observations of rapid Zn evaporation were seen on the quartz tube
above the crucible and the cooler surfaces in the area surrounding the crucible that accumulated a layer of Zn that converted to black Zn$_3$N$_2$ when exposed to the N$_2$ plasma. The introduction of N$_2$ to the plasma inhibited Zn evaporation during the ramp stage and, once the H$_2$ flow was decreased to the growth conditions, the Zn evaporation was further suppressed; the light emission from the activated Zn discharge decreased and ceased within approximately 5 seconds and the rate of deposition of Zn$_3$N$_2$ on the vicinity of the crucible greatly decreased.

To explore the issue of the suppression of Zn evaporation, we modeled the growth phase of the experiment for the two endpoint conditions where the introduction of the N$_2$ plasma 1) has no effect on Zn evaporation and 2) where it totally suppressed evaporation. The dashed curves in Fig. 2.3 show the melt composition under condition 1). These curves demonstrate that, under this condition, the temperature ramp stage would deplete the melt surface of Zn, leaving only trace amounts of Zn at the growth surface thus disallowing the growth of ZnSnN$_2$. On the other hand, suppressing the Zn evaporation averages the composition as Zn diffuses from the interior of the melt to the surface. Calculations for the case of full suppression show that the composition at the surface reached 69 % of the average composition after 5 minutes and 83 % after 10 minutes.
Table 2.1: Details of each growth experiment: date grown, product, calculated and measured melt compositions, growth temperature, duration of exposure to the nitrogen plasma, and plasma power. Uncertainties of 1 at. % in the calculated Zn composition result from an uncertainty of 50°C in the measured temperatures. Zn melt compositions are shown in at. %. Uncertainties in the EDS measurements are within 1 at. %.

<table>
<thead>
<tr>
<th>Expt.(a)</th>
<th>Product</th>
<th>Init. Zn(b)</th>
<th>Calc. Zn(c)</th>
<th>Exp. Zn(d)</th>
<th>Calc. Zn(e)</th>
<th>T(C)</th>
<th>Time(min)</th>
<th>Power(W)</th>
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<td>7/9/2011</td>
<td>Zn(_3)N(_2)</td>
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<td>18.3</td>
<td>19.1</td>
<td>9.9</td>
<td>409</td>
<td>43</td>
<td>240</td>
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<tr>
<td>7/6/2011</td>
<td>Zn(_3)N(_2)</td>
<td>24</td>
<td>18.0</td>
<td>16.1</td>
<td>9.4</td>
<td>415</td>
<td>36</td>
<td>240</td>
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<tr>
<td>5/18/2011</td>
<td>Zn(_3)N(_2)</td>
<td>22.1</td>
<td>8.7</td>
<td>5.9</td>
<td>3.1</td>
<td>439</td>
<td>60</td>
<td>240</td>
</tr>
<tr>
<td>10/3/2011</td>
<td>Zn(_3)N(_2)</td>
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<td>4.0</td>
<td>0.6</td>
<td>1.1</td>
<td>463</td>
<td>53</td>
<td>240</td>
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<tr>
<td>5/25/2011</td>
<td>ZnSnN(_2)</td>
<td>17.3</td>
<td>9.4</td>
<td>12.6</td>
<td>3.7</td>
<td>453</td>
<td>50</td>
<td>60</td>
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<tr>
<td>10/18/2011</td>
<td>ZnSnN(_2)</td>
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<td>14.6</td>
<td>8.0</td>
<td>4.0</td>
<td>497</td>
<td>61</td>
<td>240</td>
</tr>
<tr>
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<td>ZnSnN(_2)</td>
<td>21.6</td>
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<td>1.6</td>
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<tr>
<td>10/8/2011</td>
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<td>28.2</td>
<td>8.2</td>
<td>4.2</td>
<td>1.9</td>
<td>542</td>
<td>20</td>
<td>240</td>
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<tr>
<td>2/12/2012</td>
<td>Zn(_3)N(_2)</td>
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<td>4.1</td>
<td>2.5</td>
<td>2.5</td>
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<tr>
<td>9/8/2011</td>
<td>Sn(_3)N(_4)</td>
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<td>0.0</td>
<td>440</td>
<td>60</td>
<td>240</td>
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<td>11/5/2011</td>
<td>Sn(_3)N(_4)</td>
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<td>0.0</td>
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<td>1260</td>
<td>240</td>
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<tr>
<td>8/27/2011</td>
<td>Sn(_3)N(_4)</td>
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<td>0.0</td>
<td>0.0</td>
<td>560</td>
<td>855</td>
<td>240</td>
</tr>
</tbody>
</table>

\(a\) Date grown.  
\(b\) Initial melt composition.  
\(c\) Average melt composition after growth, calculated assuming that the Zn evaporation is fully suppressed at the onset of exposure to the nitrogen plasma.  
\(d\) Average melt composition after growth, measured by EDS.  
\(e\) Average melt composition after growth, calculated assuming that the Zn evaporation is not suppressed.
Table 2.1 contains the modeled post-growth Zn compositions, averaged across the melt, for the experiments described here. Also provided are the experimentally determined post-growth Zn compositions of cross-sections of the alloy charges, measured by EDS, along with the duration of the growth stage. In most cases, the experimentally determined composition falls between the two calculated data points, consistent with the observed suppression of Zn evaporation. However, this suppression was not complete and therefore as growth duration and temperature were increased, the post-growth measured composition moved farther from the zero-evaporation endpoint.

How does the $N_2$ plasma inhibit Zn evaporation? The formation of a solid nitride at the surface will obviously inhibit evaporation, but we speculate that suppression also occurs prior to supersaturation. The N that dissolves into the melt and the N at the surface must coordinate with the metal atoms, especially N with Zn since they differ in electronegativity more than N does with Sn. This metal-gas system will deviate strongly from Raoult's Law, which states that the vapor pressure of a system is equal to the sum of the vapor pressures of the components of the system multiplied by their molar fraction. In other words, the atomic N coordinates with the metal atoms forming distinct complexes that prevent the atomic N from recombining into $N_2$. These complexes lower the vapor pressure of the metal-gas matrix.
2.3 Summary of results

In Figure 2.4 we chart the material yielded at a given temperature and post-growth Zn composition. The highest temperature growth that yielded Sn₃N₄ underwent an extended cleaning phase that evaporated all of the Zn prior to growth. We surmise that ZnSnN₂ did initially grow at 505 °C but sublimated into Sn₃N₄ after the melt was fully depleted of Zn, due to the extremely long growth duration. The Sn₃N₄ grown at 440 °C resulted from an experiment done on a pure Sn melt.

![Figure 2.4. Material yielded as a function of temperature and alloy composition, measured by EDS. Zn₃N₂ is represented by blue circles, ZnSnN₂ black triangles and Sn₃N₄ red squares. The two ZnSnN₂ samples labeled with asterisks were grown with a plasma power of 60 W. All others were grown using 240 W.](image)
When Zn is present in the melt, the situation is more complex and experiments yielded either Zn\(_3\)N\(_2\) or ZnSnN\(_2\). Fig. 2.4 shows two temperature regimes where ZnSnN\(_2\) grew between 453 and 542 °C for compositions of 1.5 to 15 at. % Zn, and Zn\(_3\)N\(_2\) grew at lower temperatures. The presence of Zn in the melt allows for either of the Zn-containing nitrides to precipitate from the melt but it also allows for an alternative growth mechanism since there is an abundant quantity of Zn vapor at the surface of the melt. As stated in section 2.2.4, Zn\(_3\)N\(_2\) did grow in the vapor and deposit on the chamber surfaces. Likewise, some Zn\(_3\)N\(_2\) could redeposit on the melt surface where it may or may not dissociate, depending on the temperature and composition of the melt, and on kinetic barriers.

This vapor growth mechanism provides an alternative to the implausible picture that both compounds precipitate from the melt, which implies a significant shift in energetic stability between Zn\(_3\)N\(_2\) and ZnSnN\(_2\) over a small temperature span of around 60 °C, only 5 meV in energetic terms, in a small range of composition. Indeed, if the parameter space of Fig. 2.4 is near a transition point in energetic stability between the two compounds, we would expect a mixture of the two phases. However each material is single phase; AES analysis shows no experimental signature of Sn in measurements of the top and the cross-sectional area of the Zn\(_3\)N\(_2\) samples. Rather, it is more likely that the ZnSnN\(_2\) precipitates from the melt and Zn\(_3\)N\(_2\) grows in the vapor and redeposits on the melt surface and does not convert to ZnSnN\(_2\) because of kinetic barriers.
In the case of ZnSnN$_2$, growth from the vapor is not possible because of the negligible vapor pressure of Sn. Notably, ZnSnN$_2$ did form in this Zn$_3$N$_2$ regime at 450 °C. This is one of the two growths done at a plasma power of 60 W (labeled with asterisks in Fig. 2.4), rather than at 240 W. Spectroscopic emission measurements of the plasma showed a decrease in the density of N$_2^*$ by a factor of 2.3 at this lower power. ZnSnN$_2$ likely forms at these conditions because of an insufficient amount of activated nitrogen to maintain the Zn$_3$N$_2$ deposition process.

The most important factor in the competing energetic stability of two compounds with similar bonding characteristics and band gaps is the 0 K enthalpy of formation since entropic contributions to the Gibbs formation energy for both compounds are very similar. There are two theoretical inquiries into the issue of the relative stability of Zn$_3$N$_2$ and ZnSnN$_2$ that are the most insightful for a comparison of the two compounds because they report the relative enthalpies of formation of each compound in the same work, and each set of calculations used a consistent method and systematics for both materials. Reference 24 reports an enthalpy of formation for ZnSnN$_2$ that is 43% less exothermic than Zn$_3$N$_2$, at -0.07 eV/atom for Zn$_3$N$_2$ and -0.04 eV/atom for ZnSnN$_2$. On the other hand, Ref. 25 reports a value for ZnSnN$_2$ that is 300% more exothermic than Zn$_3$N$_2$, at -0.14 eV/atom for Zn$_3$N$_2$ and -0.42 eV/atom for ZnSnN$_2$. The latter value for ZnSnN$_2$, calculated by a LMTO method, has recently been revised to -0.184 eV/atom [22], which suggests a revised enthalpy of formation for Zn$_3$N$_2$, based on the relative ratio of the original values, of -0.06 eV/atom.
One experimental measurement of the enthalpy of formation of Zn$_3$N$_2$ in the literature determined a value of -0.04 eV/atom [26], in good agreement with the calculations. The only other measured value gave -0.2 eV/atom [27]. This latter value is five times more exothermic than the result of Ref. 26 and may be the result of ZnO contamination, which must be carefully accounted for given the propensity of Zn$_3$N$_2$ to convert to ZnO. There have been no reported measurements of the energy of formation of ZnSnN$_2$.

Finally, with regards to the discussion of the relative stability of Zn$_3$N$_2$ and ZnSnN$_2$, we highlight that the experimental observations of the rather robust stability of ZnSnN$_2$, compared to Zn$_3$N$_2$, seen in both the combinatorial growth experiments of Fioretti et al. and the work described in this section, along with the enthalpy of formation calculations done by Lambrecht and Punya, support the qualitative observation of Goryunova and Parthe that the stability of a ternary compound increases with the stability of its binary base compounds [28].
References


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3. Characterization of ZnSnN$_2$

3.1 Background

All XRD measurements of ZnSnN$_2$ have yielded wurtzitic spectra [1-9]. The authors of Ref. 2 proposed the Pna2$_1$ lattice for their material based on certain broad XRD peak widths that they interpreted to indicate peak splittings [2], which arise from deviations in the ratios of the lattice parameters of the Pna2$_1$ phase from the ideal wurtzite ratios. However, they did not observe the expected superlattice peaks associated with that phase. In addition, XRD peak broadening is not a good indication of ordering since peak broadening can also be caused by inhomogenous strain and grain size effects.

Fioretti, Tamboli and colleagues state that they observe Pna2$_1$ phase identifying peak splitting in their ZnSnN$_2$ grown by RF sputtering at 280 °C [8,9]. However this interpretation does not agree with predictions from theory. All predictions agree that the ratio of the lattice parameters of Pna2$_1$ ZnSnN$_2$ in the a-b plane is close to unity, and, thus, the predicted peak splitting in ZnSnN$_2$ is very small. Lahourcade et al. predict the splitting of the peaks with Pna2$_1$ Miller indices of (120) and (200) to be only 0.09 degrees [2]. The authors of Refs. 8 and 9 propose a splitting of 1.1 degrees for the (120) and (200) peaks based on their data.
Samples of ZnSnN$_2$ reported in the literature can be separated into two categories: ZnSnN$_2$ grown above and below 450 °C. Most samples grown below 450 °C do not exhibit photoluminescence and have either free carrier concentration dependent band gaps that are affected by the Burstein-Moss mechanism, that is an increase in the onset of photon absorption due to conduction band filling, or disorder-induced low band gaps, relative to ordered ZnSnN$_2$. In this thesis we report on samples of ZnSnN$_2$ grown above 450 °C by the VLS method that exhibit room temperature and 77 K photoluminescence [3,10]. We derive a band gap of 1.7 eV from these PL data that is equivalent to the band gap for ordered ZnSnN$_2$ given by accurately predictive band gap calculations [10]. These PL and PLE measurements will be discussed further in section 3.2.2.

There are a few exceptions to the two categories described above. Two samples of ZnSnN$_2$ grown by plasma-assisted MBE at 450 and 500 °C have band gaps of 2.21 and 2.18 eV, and free electron densities of 1.2 x 10$^{20}$ and 1.4 x 10$^{19}$ cm$^{-3}$, respectively [1,11]. Zn-rich samples of Zn$_{1-x}$Sn$_x$N grown by RF sputtering around 300 °C, exhibit PL at 4.25 K in the range of 1.35 - 1.5 eV [8].

In the remainder of this introductory section we describe the ZnSnN$_2$ samples grown below 450 °C in greater detail.

Lahourcade et al. grew two samples of ZnSnN$_2$ at 250 °C using RF sputtering [2]. The sample grown on c plane sapphire exhibited a band gap of ~1.9 eV, measured
by absorption spectroscopy, and a free carrier concentration of \( \sim 5 \times 10^{19} \text{ cm}^{-3} \). The second sample, grown on c plane GaN, had an absorption onset at \( \sim 2.2 \text{ eV} \) and free carrier concentration of \( \sim 1 \times 10^{21} \text{ cm}^{-3} \). In both cases, the authors of Ref. 2 proposed that the absorption edge is elevated to higher energies from the fundamental gap by the Burstein-Moss effect.

Veal et al. grew ZnSnN\(_2\) using plasma-assisted MBE at 400 \(^{\circ}\)C with a Zn:Sn flux ratio of 39:1 and a \( \text{N}_2 \) pressure of \( 2 \times 10^{-5} \text{ torr} \) that has an absorption onset of 1.33 eV and a free electron density of \( 2.7 \times 10^{20} \) \([11]\). Material grown under the same conditions but with a Zn:Sn flux ratio of 36:1 gave an absorption onset of 2.12 eV and a free electron density of \( 1.1 \times 10^{21} \). The same group grew another sample at 400 \(^{\circ}\)C and at the 36:1 Zn:Sn flux ratio but with a \( \text{N}_2 \) pressure of \( 1 \times 10^{-5} \text{ torr} \) that exhibited an absorption onset at 2.38 eV and a free carrier concentration of \( 3.0 \times 10^{20} \).

Deng et al. grew samples of ZnSnN\(_2\) at room temperature using DC magnetron sputtering \([6]\). Their as-grown sample exhibited an absorption onset at 1.82 eV. Annealing their samples in \( \text{N}_2 \) at atmospheric pressure at 300 and 400 \(^{\circ}\)C for 3 hours increased the gaps to 1.92 and 1.95 eV, respectively. Hall effect measurements showed a decrease in carrier concentration from \( 1.6 \times 10^{18} \) to \( 2.3 \times 10^{17} \text{ cm}^{-3} \) with annealing. Interestingly, the carrier mobility also decreased as the annealing temperature was raised, from 3.98, for the as-grown sample, to 1.86 cm\(^2\) V\(^{-1}\) s\(^{-1}\), for the sample annealed at 400 \(^{\circ}\)C.
Fioretti et al. used a combinatorial RF sputtering technique to grow Zn$_{1-x}$Sn$_x$N under many different conditions [8]. The material yielded from these experiments was either Zn-rich, Sn-rich or stoichiometric ZnSnN$_2$, as measured by x-ray fluorescence spectroscopy. Stoichiometric and Sn-rich material had free carrier concentrations on the order of $1 \times 10^{20}$ cm$^{-3}$. Zn$_{0.60}$Sn$_{0.40}$N grown at 380 °C had a free concentration of $3 \times 10^{18}$ cm$^{-3}$. A summary of their results shows a carrier density dependent absorption edge between ~ 0.9 and 1.35 eV.

The authors of Ref. 8 proposed that their material is highly disordered with a band gap of ~ 1.0 eV and that the absorption edge was increased in some samples due to the Burstein-Moss effect. Observations of the Burstein-Moss effect were also reported in Refs. [1,2,4,5,7-9].

Fioretti et al. annealed their ZnSnN$_2$ at 300 °C, in an activated N$_2$ plasma [9]. Deng et al. also annealed their ZnSnN$_2$ at 300 and 400 °C, in N$_2$, [6]. In both sets of annealing experiments, it was reported that annealing lowered the conductivity and mobility of their samples, and increased the free carrier concentrations. The authors of Ref. 9 speculated that annealing resulted in a clustering of octet-rule-violating defects into charged ‘motifs’ with high scattering factors, which led to the observed effects [12].

The effect of annealing ZnSnN$_2$ in an environment that does not contain Zn should be further investigated. As described in section 2.3 of this thesis, we observed the
conversion of ZnSnN$_2$ to Sn$_3$N$_4$ in a Zn-free environment at temperatures near 500 °C, presumably due to the sublimation of Zn.

The proposition that the band gap of ZnSnN$_2$ can be decreased through a cation-disorder induced mechanism is based on first principles calculations of perfectly random, stoichiometric ZnSnN$_2$ by the special-quasi-random (SQS) method. This SQS method is based on an ensemble of periodic supercells with atomic arrangements that mimic randomness. In the case of isovalent binary alloys, a random cation distribution does not generate octet rule violations and the SQS method has been very successful [13]. For the heterovalent ternaries, a random distribution of cations results in a high density of octet rule violations. The calculations in Ref. 4 predict a dramatic decrease in the band gap for ZnSnN$_2$, from 2 eV in the case of a fully ordered Pna2$_1$ structure, to 1 eV for a structure for which the cations are placed randomly.

We may gain insight into the issue of disorder in ZnSnN$_2$ by considering theoretical results for the zincblende-based ternary semiconductors, which are closed related to the wurtzite-based ternaries. The zincblende-based ternaries are predicted by first principles calculations to form high densities of two charge-neutral defect complexes related to the group II atom vacancy and cation exchange, for instance (Zn$_{Sn^{-2}}$ + Sn$_{Zn^{+2}}$) [14,15,16]. In CuInSe$_2$, the defect complex (In$_{Cu^{2+}}$ + 2V$_{Cu^{-}}$) is the lowest energy defect [14]. Indeed, group II vacancies have been observed by electron paramagnetic resonance in ZnGeP$_2$ [17] and CdSiP$_2$ [18]. It is possible that
off-stoichiometric ZnSnN$_2$ also forms charge-neutral Zn-vacancy related defect structures.

3.2 Characterization of ZnSnN$_2$ grown by VLS

3.2.1 Experimental Details

The material used for the measurements reported here was grown at 485 °C from a melt with a starting composition of 25 at. % Zn. Polycrystalline ZnSnN$_2$, with estimated average thicknesses of 250–350 nm, formed on top of the melt, as shown in the scanning electron microscope (SEM) image in Fig. 1. Auger chemical analysis showed equal ratios of Zn and Sn within an experimental uncertainty of 1 %, based on the signal noise (Fig. 2.2).
X-ray diffraction was taken on the as-grown sample using an X-ray diffractometer with Cu Kα (1,2) irradiation at small incident angle, focused to a 500 μm diameter spot size at the sample, and using a two dimensional xenon detector with a step size of 0.02°.

The room temperature PL and Raman spectra were taken in ambient atmosphere using a continuous-wave (CW) HeNe at 1.96 eV and a CW solid-state laser at 2.33 eV. The lasers were focused onto the sample to 1–2 μm diameter spot sizes by a ×50 objective. The radiation from the sample was collected by the same objective, passed through appropriate filters, and dispersed by a grating spectrometer equipped with a liquid-nitrogen cooled silicon charge-coupled-detector.
Photoluminescence excitation (PLE) spectra were taken with a supercontinuum fiber laser with a repetition rate of 40 MHz and pulse duration of a few picoseconds, using the optical setup described above for the PL measurements. Excitation radiation from 1.55 to 2.76 eV was wavelength-selected using a series of tunable filters. The peak intensity at the sample surface was kept below $1.5 \times 10^8$ W/cm$^2$. Two filters were used to select two different portions of the PL spectrum, one from 1.65 to 1.68 eV, and another from 1.31 to 1.42 eV.

The excitation source for the measurement of the PL spectrum at 77 K was a 633 nm He-Ne laser with incident intensity of 10.6 kW/cm$^2$ and a spot size with a 40 μm diameter.

### 3.2.2 Results and Discussion

The XRD spectrum shown in Fig. 3.2 was obtained from the material pictured in Fig. 3.1. The average crystallite size, estimated from the (200)/(120) peak width using the Scherrer formula, is approximately 70 nm, consistent with the crystallite sizes discernible in the SEM image (Fig. 3.1). The fitted orthorhombic lattice parameters are listed in Table I along with the predicted values from Ref. 20. Two simulated powder diffraction spectra are shown in Fig. 3.2 as well, one for a wurtzite lattice, calculated by setting the occupation probabilities of Zn and Sn each to $\frac{1}{2}$ on the group III wurtzite sublattice, and the other for the Pna2$_1$ lattice, which is predicted to be the most energetically stable phase. The absence of any
peaks in the measured XRD spectrum unique to the calculated Pna2₁ structure is consistent with the presence of disorder on the II–IV orthorhombic sublattice, yielding a ‘wurtzite-like’ XRD spectrum.

Figure 3.2 (taken from Ref. 3). Measured and calculated X-ray powder diffraction spectra [19]. The peaks labeled # and * are from Sn and Zn, respectively. The Miller indices labeling the experimental peaks are for the Pna2₁ phase.
Table 3.1 (taken from Ref. 3). Comparison of the experimentally determined lattice parameters with calculated lattice parameters from Ref. 20.

<table>
<thead>
<tr>
<th></th>
<th>Calculated (Å)</th>
<th>Experimental (Å)</th>
</tr>
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<tbody>
<tr>
<td>$a$</td>
<td>5.85</td>
<td>5.842 ± 0.007</td>
</tr>
<tr>
<td>$b$</td>
<td>6.76</td>
<td>6.753 ± 0.006</td>
</tr>
<tr>
<td>$c$</td>
<td>5.58</td>
<td>5.462 ± 0.003</td>
</tr>
</tbody>
</table>

The measured PL spectrum is shown in Fig. 3.3. The PL peak is near 1.5 eV. We note that the shape of the PL spectrum was observed to be independent of the excitation energy over the entire range of excitation intensity, from $10^3$ to $10^6$ W/cm$^2$.

The band gap was determined using PLE. The PLE spectrum shown in Fig. 3.3 was generated by integrating the PL intensity in the two photon-energy regions labeled by 1 and 2. This PL intensity was normalized by the excitation photon flux as a function of the excitation photon energy in the range of 1.55 to 2.76 eV. The two inverted triangles were taken using the two CW lasers, at intensities of approximately 1 kW/cm$^2$. All other data were obtained using the picosecond light source with peak intensities approximately 5 orders of magnitude higher than for the CW measurements. For excitation intensities below 100 W/cm$^2$, the PL efficiency was observed to decrease as the excitation intensity was reduced, indicating that recombination through nonradiative channels became more important at these lower excitation intensities.
The solid curve in Fig. 3.3, obtained by fitting the function \((E - E_g)^p\) to the PLE spectrum of the higher-energy PL, yields a band gap \(E_g = 1.7 \pm 0.1\) eV, for various values of \(p\), with the best fit \(p = 0.73 \pm 0.04\). This phenomenological fit is consistent with an absorption coefficient that reflects a square-root density of states, characteristic of a direct gap, combined with exciton enhancement of the absorption near the band gap.
The PL peak at 1.5 eV was identified as defect luminescence, and the gap measured by PLE spectrum as the intrinsic gap [3]. At 77 K the defect peak is still evident (Fig. 3.4(a)), but the PL spectrum is dominated by the near-band-edge peak centered at approximately 1.72 eV [10]. The relative increase in the near-band-edge luminescence at the lower temperature is a commonly observed phenomenon that results from a decrease in the thermal velocity of the carriers that slows the transfer of photoexcited carriers to the defect states responsible for defect luminescence. Figure 3.4(b) shows the dependence of the defect and near-band-edge peak intensities as a function of excitation intensity, with the defect peak height normalized to that of the near-band-edge peak at the lower range of excitation intensity, in order to best compare the dependence of the two peak intensities on excitation intensity. At lower excitation intensity the dependence is linear, while at higher intensity the dependence becomes superlinear, an indication that defect recombination channels are becoming saturated at this still-low range of excitation intensity.
Figure 3.4 (taken from Ref. 10). (a) Photoluminescence spectrum of ZnSnN$_2$ at 77 K. The peak at 1.72 eV is near-band-edge recombination. The peak at 1.5 eV is the same defect peak seen in Fig. 3.3. (b) Photoluminescence peak intensities versus incident intensity. The defect peak intensity at 1.5 eV has been scaled to the peak intensity of the 1.72 eV near-band-edge peak intensity at low excitation intensities.
An alternative interpretation of our data is that the 1.7 eV absorption edge that we measured by PLE at 300 K is increased from the fundamental gap by band gap filling. In this picture, the PL peak at 1.5 eV is due to excited carriers relaxing to the valence band from the conduction band minima, at 1.5 eV, and the measured absorption onset is increased to the Burstein-Moss effect. However, this interpretation cannot explain the origins of the PL peak observed at 1.7 eV in the 77 K data. This PL peak must be due to the relaxation of photoexcited electrons from the minimum of the conduction band to either defect bands or to the valence band maximum. The most likely scenario is that the PL peak that appears at 77 K strongly supports the 1.7 eV fundamental band gap interpretation derived from our room temperature PLE data and demonstrates that the Burstein-Moss effect is not present in our material.

Additional evidence of a 1.7 eV band gap is provided by first principles calculations done in Ref. 20. These calculations predict a zero temperature band gap of 2.02 eV calculated using a QSGW method, and 1.8 ± 0.1 eV using QSGW and our measured lattice parameters. The latter is in particularly close agreement with our measured value of the band gap at room temperature, especially considering that we expect a shift to lower energy of the order of 100 meV for T = 300 K.

We now return to the results of calculations and measurement of the Raman spectrum of ZnSnN$_2$. The calculated Raman spectrum in Fig. 3.5(a) was obtained by adding the calculated intensities of all modes ($a_1$, $b_1$, $b_2$, and $a_2$), with equal
weights, taken from Paudel and Lambrecht [21]. This spectrum is dominated by a peak at approximately 590 cm$^{-1}$, identified with a wurtzite-$E_2$-high-like vibrational pattern. The measured Raman spectrum of Fig. 4(b) shows none of the predicted Raman peaks, not even the dominant one.

The experimental spectrum is phonon-glass-like, showing complete breakdown of the $\mathbf{k}$-vector selection rule. This result is consistent with the x-ray-diffraction results showing a highly disordered lattice. However, neither the XRD or Raman spectra give information on the type of disorder.

Thus, the type of disorder present in our material does not seem to have a significant effect on the measured band gap. This interpretation is in sharp contrast to the prediction of SQS theory. It follows that the disorder is not octet-rule-violating. In the next chapter we will present a model of disorder in ZnSnN$_2$ that is consistent with the above observations.
Fig. 3.5 (taken from Ref. 10). Raman spectra and calculated phonon density of states of ZnSnN$_2$. Calculated (a) and measured (b) Raman spectra and calculated density of states: (c) Gaussian broadened and (d) high resolution [21].
References


4. Cation disorder in wurtzite-based heterovalent ternary compounds

4.1 Introduction

Chapter 3 showed that, in ZnSnN$_2$, disorder so greatly disrupts periodicity on the cation sublattices that XRD superstructure is washed out and momentum selection rules appear to be broken for Raman spectra. In the material reported on in this thesis, disorder seems to minimally affect the band gap. Disorder by a random array of cations cannot explain these observations because that type of disorder involves many octet rule violations that should decrease the gap, according to calculations. How can these XRD, Raman and PL observations be reconciled? This chapter seeks to address that question.

In section 4.2, we show that octet-rule-satisfying mixtures of the Pna2$_1$ and Pmc2$_1$ phases can be described by a pseudospin model. This treatment parallels the appendix of Ref. 1, which shows that all octet-rule-satisfying mixtures of the Pna2$_1$ and Pmc2$_1$ phases can be described by a pseudospin model, with the exception of a highly symmetric twinned structure. We show that simulated XRD spectra of these structures, even with a small amount of mixing, have superstructure peak intensities much too dim to have been measured in the cases reported to date [1]. In section 4.3, we discuss the more realistic case in which the constraint of the
strict preservation of the octet rule is relaxed. Following a similar method to the one used in the appendix of Ref. 1, we explore the affect of the Zn-Sn exchange defect on the Pna2₁ lattice.

4.2 Cation disorder without octet rule violations

The appendix of Ref. 1 demonstrates that, in the case of the wurtzite-based heterovalent ternaries, the Pna2₁ and Pmc2₁ phases can mix in such a way that the octet rule is preserved. We show in Fig. 4.1(b and c) that some of the rows of cations in both the Pna2₁ and Pmc2₁ phases have ABAB periodicity, as do the rows of cations along the a axis in the Pna2₁ structure. Thus, the Pna2₁ and Pmc2₁ structures can be obtained by stacking such rows along the b axis. We define the s = ±1 pseudospin layers as shown in Figs. 4.1(d and e). The dashed lines outline primitive cells of the Pmc2₁ structure. We can clearly see that the two layers are mirror images of each other. The Pna2₁ structure results from +1, −1 stacking of these pseudospin layers along the Pna2₁ b axis, and the Pmc2₁ structure results from +1,+1 or −1,−1 stacking. It follows that an infinite number of polytypes can be built from larger repeat units. The appendix of Ref. 1 shows rigorously that the only ternary crystal structures based on the wurtzite lattice that preserve local charge neutrality are those described by sequences of the ±1 pseudospin layers, with the sole exception of the structure shown in Fig. 1(f). This unique structure is a sixfold twinning of the Pmc2₁ crystal structure about the central out-of-plane axis of the figure. The dashed lines show the interfaces between the six planes.
Figure 4.1. Projection of some ABC$_2$ crystal structures on the c plane. Large spheres are the cations, small spheres are the anions. a) Pna$_2$$_1$, b) Pmc$_2$$_1$ rotated from the orientation of Fig. 1.1 counterclockwise by 120°, c) Pmc$_2$$_1$ rotated clockwise by 120°. c) and d) define the +1 and -1 pseudospin layers. e) The octet-rule-preserving twinned structure. The twin boundaries are shown by the dashed lines.
A major contribution to the free energy is the energy of formation, which is expressed for a crystal of \( N \) pseudospin layers in terms of the layer interactions:

\[
E = E_0 + \frac{1}{N} \sum_{n=1}^{M} \sum_{i=1}^{N-1} J_n S_i S_{i+n}
\]

(1)

Here the \( J_n \) are the energies of interaction between the \( n \)th nearest-neighbor spin layers, with a range up to \( M \), and \( E_0 \) is a convenient reference energy. The spins here are isospins pointing up or down.

Reference 1 reported a difference in the calculated energies of formation \((J_1)\) for the \( \text{Pna}_2\text{I} \) and \( \text{Pmc}_2\text{I} \) phases of only 6.5 \( \pm \) 1.5 meV/fu. So in ZnSnN\(_2\), we assume that interaction energy terms \( J_n \) with \( n \) greater than one are negligible.

Accordingly, we expect a high degree of mixing of the two phases due to the similar formation energies of \( \text{Pna}_2\text{I} \) and \( \text{Pmc}_2\text{I} \). A very rough estimate of the degree of mixing is given by the Boltzmann factors for \( \text{Pna}_2\text{I} \) and \( \text{Pmc}_2\text{I} \):

\[
\frac{1}{1 + e^{-2J_1/kT}} \quad \text{and} \quad \frac{e^{-2J_1/kT}}{1 + e^{-2J_1/kT}},
\]

respectively. These give proportions for \( \text{Pna}_2\text{I} \)- and \( \text{Pmc}_2\text{I} \)-type stackings of 55 \% and 45 \%, at 450 °C.

We followed the formulation of Kopp, Schmidbauer and colleagues to calculate analytically the x-ray-diffraction spectra for a ZnSnN\(_2\) crystal with one-dimensional disorder due to random stacking along the \( \text{b} \) axis [2], as a function of the total thickness of the crystal and as a function of the proportion of \( \text{Pna}_2\text{I} \) to
Pmc\(_2\)\(_1\) stacking [1]. This is a transfer matrix method that generates an analytical solution equivalent to a Monte Carlo generation of the averaged diffraction peak intensities for an ensemble of crystals. The solution is specific to the case of a random distribution of stacked layers described by a stationary Markov chain; that is, the probability of layer \(i + 1\) stacking upon layer \(i\) is dependent only upon layer \(i\). In this case, the probability is determined by specifying the relative proportions of the Pna\(_2\)\(_1\) and Pmc\(_2\)\(_1\) phases.

The information required for the calculation includes the number of pseudospin layers \(N\), the probability \(N_s/N\) associated with each pseudospin type \(s = \pm 1\), the structure factors for each of the pseudospin layers, and the conditional probabilities governing the likelihood of layer \(j'\) of pseudospin character \(s_j'\) occurring after layer \(j\) with pseudospin character \(s_j\). Because the two spin states are mirror symmetric, they are equally probable, and thus \(N_{+1}/N\) and \(N_{-1}/N\) are both equal to 1/2.

The structure factors for the two pseudospin layers were calculated using the atomic form factors for Zn, Sn, and N from the International Union of Crystallography database. The atomic positions were referenced to the orthorhombic lattice parameters \(a = 0.6749\) nm, \(b = 0.5845\) nm, \(c = 0.5544\) nm and the Wyckoff positions for the ideal wurtzite lattice. The relative peak intensities were calculated using the standard Lorentz polarization factor \(L_p(\theta) = (1 + \cos^2 2\theta)/(\sin^2 \theta \cos \theta)\).
For ZnSnN$_2$ the small value of $J_1$, compared to kT at the growth temperature, is consistent with roughly equal probabilities for the two types of stacking. We now show that for ZnSnN$_2$ the measured, wurtzite-like x-ray-diffraction spectra are consistent with our ordering model. Figure 4.2 shows the calculated x-ray-diffraction spectra for ZnSnN$_2$ for four cases: for the perfectly ordered Pna2$_1$ and Pmc2$_1$ phases, for a disordered wurtzite phase for which the atomic form factor for the cations is the average of those of Zn and Sn, and for a crystal composed of 240 pseudospin layers made up of equal proportions, but random distributions, of +1 and −1 pseudospins. For ease of comparison we use the ideal wurtzite atomic positions, the lattice parameter $a = 0.671$ nm, and the ideal wurtzite ratios $b/a = \sqrt{3}$ and $c/a = \sqrt{8/3}$. The strongest superstructure peaks unique to the pure crystals, which are the (111) peak for the Pmc2$_1$ structure and the (101) peak for the Pna2$_1$ structure, are labeled. Note that these are reduced in intensity by two orders of magnitude for the 240-layer disordered crystal, compared to the perfectly ordered structures. Superstructure peaks are absent in the measured spectrum, from Ref. 3, and in the other reports of x-ray-diffraction measurements of ZnSnN$_2$ [4-11].
Figure 4.2 (taken from Ref. 1). X-ray-diffraction spectra for ZnSnN₂. From top to bottom, the calculated powder XRD spectra of ZnSnN₂ for the Pna2₁, Pmc2₁, and wurtzite crystal structures, as crystal composed of 240 pseudospin layers with a 50:50 mixture of the Pna2₁ and Pmc2₁ structures, and the measured spectrum. The starred peaks in the measured spectrum are associated with the Zn-Sn melt upon which the ZnSnN₂ was grown.

Figure 4.3(a) shows the dependence of the intensities of the superstructure peaks on the number of layers, relative to the Pna2₁ (221) peak, which is the strongest peak common to the Pna2₁, Pmc2₁, and wurtzite crystal structures. The
calculations show that the x-ray diffraction spectra in Refs. 3 and 5 have signal-to-noise ratios far too low to detect the superstructure peak intensities predicted for this model. In the first case, the depth probed is the typical Cu Kα coherence length. In the second case, the coherence length is limited by the 70-nm grain size of the polycrystalline material.

Figure 4.3(b) shows the result of a calculation of the highest intensity superstructure peaks as the proportions of the two pure phases are varied, for both a 240-layer crystal and for a 24-layer crystal. The figure also illustrates that the relative intensity of the superlattice-diffraction peak to the Pna2₁ (221) peak drops very quickly below the signal-to-noise ratio unless the stacking is nearly perfect Pna2₁ or Pmc2₁ or unless only a few layers in the crystal are sampled.
Figure 4.3 (taken from Ref. 1). Normalized x-ray-diffraction peak intensities for ZnSnN$_2$. (a) The ratio of the Pmc$_2$ (111) peak to the (221) peak for a 50:50 mixture of the Pna$_2$ and Pmc$_2$ phases as a function of the number of layers. The intensity of the (221) peak is independent of the ratio of the two phases. The two vertical dashed lines mark the number of layers that correspond to the average grain size seen in Fig. 3.1 and measured by the Scherrer equation, and the typical coherence length of a standard Cu Kα x-ray source. The two horizontal dashed lines at 0.011 and 0.02 mark the signal-to-noise ratios for the ZnSnN$_2$ x-ray-diffraction spectra reported in of Fig. 4.7 and Ref. 5, respectively. (b) The ratios of the Pna$_2$ (111) and Pmc$_2$ (101) x-ray-diffraction peaks to the (221) peak versus the fractional mixtures of the two phases, calculated for sampling depths of 24 and 240 pseudospin layers.
4.3 Cation disorder with octet rule violations

4.3.1. Introduction

One key merit of the idealized, charge-neutral model described in Section 4.2 is that violations of the octet rule have been shown to be energetically costly [1], which justifies constraining them from the model. However, in real samples, octet-rule-violating defects are most likely present even in high quality, stoichiometric material.

There are many types of native defects that can be present in real samples, including vacancies, interstitials, and antisite defects. In the zincblende-based heterovalent ternary semiconductor CuInSe₂, first-principles calculations show that two charge-neutral defect complexes, (InCu²⁺ + 2VCu⁻) and the exchange defect (CuIn²⁻ + InCu²⁺), are particularly low in formation energy [12]. Equivalent defect complexes have also been shown to be the lowest formation energy defects in ZnGeP₂ [13] and ZnSnP₂ [14].

Based on the calculations for the zincblende-based ternaries CuInSe₂, ZnGeP₂ and ZnSnP₂, we speculate that the two charge-neutral defect complexes, (SnZn²⁺ + 2VZn⁻) and (SnZn²⁻ + ZnSn²⁺), are low in formation energy in the case of ZnSnN₂. This speculation provides particular utility if we again assume that our material is perfectly stoichiometric. If we model our material as stoichiometric, than the
\[(\text{SnZn}^{2+} + 2V_{\text{Zn}}^-)\] defect complex is not present, or at least it must be accompanied by a Zn-interstitial defect that is high in formation energy relative to the charge-neutral defect complexes. Justification for the idealization of stoichiometry in our material, and in the model that we present in the remainder of this chapter, is supported by the AES spectra shown in Fig. 2.2, and the high crystalline quality suggested by the observations of room temperature PL and 77 K PL emitted at the fundamental gap. Therefore, in the following section we investigate the nature of exchange defects in the wurtzite-based heterovalent ternaries exclusively.

4.3.2 Exchange defects in the Pna2\(_1\) structure

Figure 4.4 shows a two-dimensional projection along the \(c\) axis of the Pna2\(_1\) phase with one next-nearest-neighbors exchange defect centered in the lattice. The Pna2\(_1\) background is characterized by a zigzag arrangement of cations, highlighted by the red lines in Fig. 4.4. The displaced atoms are drawn as discs (marked with white Xs) and the ground state atoms are spheres. Each cation in the exchange defect that is displaced from its ground state location generates three tetrahedra where an anion is locally surrounded by 1 \(A\) atom and 3 \(B\) atoms and three tetrahedra where an anion is locally surrounded by 3 \(A\) atoms and 1 \(B\) atom; these octet-rule violating tetrahedra are highlighted by the red and yellow anions. Four of these acceptors and donors are shown in Fig. 4.4, the remaining two (not shown) are located directly above the displaced atoms along the \(c\) axis. Due to
their proximity, these acceptors and donors will be referred to as acceptor-donor (A-D) pairs.

For comparison, we note that an isolated Zn\textsubscript{Sn} substitutional defect generates 4 acceptor octet-rule violations in the surrounding tetrahedra, and an isolated Sn\textsubscript{Zn} substitutional defect generates four donor violations.

Figure 4.4. One exchange defect embedded with the Pna\textsubscript{2}\textsubscript{1} crystal structure. Large spheres are the cations, small spheres are the anions. The large discs marked by Xs are cations displaced from their ground state locations. Small discs indicate off-stoichiometric tetrahedra. The red lines highlight patterns in the structures.

There are six possible types of exchange defects on the ternary Pna\textsubscript{2}\textsubscript{1} lattice. These defects are catalogued in appendix C.
Figure 4.5 shows two adjacent exchange defects that are close enough to bond to a common cation. Notice that the geometry of these exchange defects leads to the annihilation of an acceptor-donor pair. This is quite interesting since it strongly suggests that the formation energy of this defect cluster is less than the case of two isolated exchange defects.

Figure 4.5. Two exchange defects embedded with the Pna2₁ crystal structure. Large spheres are the cations, small spheres are the anions. The large discs marked by Xs are cations displaced from their ground state locations. Small discs indicate off-stoichiometric tetrahedra. The red lines highlight patterns in the structures.

For each of the six types of exchange defects listed in appendix C, there are 102 ways to orient an adjacent cation-exchange defect. 66 of these orientations generate 2.5 acceptor-donor pairs per exchange defect, 33 of the orientations
generate 3 acceptor-donor pairs per exchange defect, and 3 defect orientations
generate only 2 acceptor-donor pairs per exchange defect.

Figure 4.6. Four exchange defects embedded with the Pna2₁ crystal structure. Large spheres are the cations, small spheres are the anions. The large discs marked by Xs are cations displaced from their ground state locations. Small discs indicate off-stoichiometric tetrahedra. The red lines highlight patterns in the structures.

The number of acceptor-donor pairs per exchange defect further decreases as the clusters increase in size. In Fig. 4.6, four exchange defects congregate in a chain along the a axis. In this case, there are only 2.25 acceptor-donor pairs per exchange defect. It can be easily shown that, for exchange defects aligned along the a axis, the number of acceptor-donor pairs per exchange defect equals, 2 + \( \frac{1}{\text{number of exchange defects}} \), which suggests that there is an energetic benefit to the clustering of exchange defects.
We picture in Fig. 4.7 one of the special orientations of two exchange defects that generates only 2 acceptor-donor pairs per exchange defect. Defect pairs arranged along the c axis in the manner shown in Fig. 4.7 generate only $1 + 2/\text{number of exchange defects}$ acceptor-donor pairs per exchange defect, and are thus, presumably, significantly lower in formation energy than the same number of isolated non-interacting exchange defects.

Figure 4.7. Two exchange defects embedded with the Pna2$_1$ crystal structure. Large spheres are the cations, small spheres are the anions. The large discs marked by Xs are cations displaced from their ground state locations. Small discs indicate off-stoichiometric tetrahedra. The red lines highlight patterns in the structures.

As a final note on the interesting characteristics of cation exchange defects in the wurtzite-based ternaries, we highlight the line tracing the cation pattern through the cluster of four defects shown in Fig. 4.6. The arrangement of atoms highlighted
by the straight line is characteristic of the second, excited Pmc2₁ phase (Fig. 4.1). 
Thus, certain cluster arrangements of exchange defects are equivalent to sections of Pmc2₁ embedded within the ground state Pna2₁ lattice.
References


5. Summary and outlook

Here we explored the Zn-Sn-N system by a VLS method, which consists of providing activated N₂ to the surface of a Zn - Sn alloy melt. We found that ZnSnN₂ can be synthesized as high quality material that is photoluminescent at room temperature. Each of the compounds Zn₃N₂, Sn₃N₄ and ZnSnN₂ can form in single phase by varying the melt composition and growth temperature. ZnSnN₂ precipitated from the melt between 453 and 542 °C, at alloy compositions from 1.5 to 14 %. The formation of ZnSnN₂ at these conditions suggests that ZnSnN₂ has a lower enthalpy of formation than Zn₃N₂, in contrast to a prediction from theory.

The ordering model described here provides an explanation for how cation disorder in ZnSnN₂ can be present in material that has a band gap that is unchanged from the gap predicted by theory for fully ordered material. We have shown that all atomic arrangements that do not violate the octet rule, with one notable exception, can be described by a pseudospin model formed from the common ABAB basal plane that occurs in the Pna2₁ and Pmc2₁ crystal structures. Based on first-principles calculations, the Pna2₁ and Pmc2₁ phases have nearly the same band gap for ZnSnN₂, which can explain why a mixture of the two phases does not substantially change the band gap of the material.

The strict constraint of the octet rule is a useful idealization that allows for us to
analytically calculate the XRD spectra of mixtures of the Pna\textsubscript{2} and Pmc\textsubscript{2} phases. However, in real material, there are certainly small numbers of defects that generate octet rule violations. One interesting type of defect is the cation exchange defect. We have shown here that groups of exchange defects can form portions of the Pmc\textsubscript{2} phase embedded within the Pna\textsubscript{2}. This variation of the phase mixing model is worth exploring as an alternative to the octet rule fulfilling model because the exchange defects or clusters of exchange defects can occur anywhere on the three-dimensional lattice, and thus introduce a three-dimensional entropy term. This three-dimensional entropy contribution is in contrast to the pseudospin model, where configurational entropy is dependent only on the number of pseudospin layers and is, therefore, one-dimensional.

The results described in this thesis will inform future growth studies of ZnSnN\textsubscript{2}. Furthermore, this work is a step towards a better understanding of disorder in ZnSnN\textsubscript{2} and other wurtzite-based ternary semiconductors, which may allow researchers to account for cation disorder in device designs and tailor device designs in order to utilize disorder.
Appendix A

The rapid evaporation of Zn from the growth melt makes it is necessary to minimize the H\textsubscript{2} plasma cleaning time prior to synthesis. This task is made more difficult by the robust tin oxide and zinc oxide contaminants that dissociate slowly under an H\textsubscript{2} plasma. Indeed, attempts to remove the oxides from a melt consisting of zinc and tin shot that was simply loaded and alloyed within the growth chamber not only failed to remove the oxides, but failed to alloy the two metals because the zinc oxide shell on the zinc shot remained intact. For these reasons, we refined the tin and zinc shot of their native oxides and alloyed the two metals using graphite crucibles within a N\textsubscript{2} glovebox prior to loading into the growth chamber.

The crucibles used in the metal refining and alloying procedure were machined from graphite because the carbon can interact with the oxides to form CO\textsubscript{2}. The action of the graphite to dissociate the tin oxide was seen on the refined tin, which was specular and metallic where it was in contact with the graphite crucible. We are uncertain which phase of tin oxide was present on our metal and we did not analyze the tin in depth to determine the tin oxide phase. The native oxide on the tin shot was colorless, indicating that it is SnO\textsubscript{2}. However, the oxide seen on the top of the refined Sn and in small quantities on the alloyed growth charge did have a reddish tint, which is indicative of the metastable SnO phase. It is possible that the high refining temperatures and the action of the graphite converted the SnO\textsubscript{2} into SnO or that both tin oxide phases were present together.
The principle underlying these refining and alloying procedures is that both tin and zinc oxide are less dense than the pure metals. Both SnO₂ - 6.95 g/cm³ - and SnO - 6.45 g/cm³ - are less dense than Sn - 7.365 g/cm³, and ZnO - 5.606 g/cm³ - is less dense than Zn - 7.14 g/cm³. Therefore, by melting the metals and oxide layers, the oxides will float to the melt surface, leaving refined metal to be removed from the bottom after cooling.
Fig. A1. Zn and Sn refining and alloying hardware. A – Sn refining outer housing, B – tapered Sn refining bottom crucible, C – Sn refining top crucible, D – Zn refining top crucible, E – tapered Zn refining bottom crucible, F – Zn refining outer housing, G – Alloying bottom plate, H – Alloying crucible, I – Alloying top, J – tongs, K - 70 x 50 Pyrex dish (#3140) and 150 mL Pyrex beaker (#1000), L – long-handled tweezers, M – wire clippers.

Preparing the growth charge.

Refining the metals.

1. Load all tools (Fig. A1) and metal shot into the glovebox.

2. First insert the Sn refining bottom crucible (B), then the crucible top (C), into the Sn refining housing (A).
   a. Load B and C with Sn shot.

3. Insert the Zn refining bottom crucible (E) into the Zn refining housing (F), followed by the top crucible (D).
   a. Load E and D with Zn shot.
The filled Sn and Zn refining crucibles are pictured in Fig. A2(N) and Fig. A2(O), respectively.

4. Place each metal refining crucible inside the 70 x 50 Pyrex dish (#3140) and cover with the 150 mL Pyrex beaker (#1000). This assembly is shown in Fig. A1 (K). Position on the hot plate as shown in Fig. A2.

5. Turn on the hot plate to the maximum power (approximately 450 °C at the hot plate surface).

For the remaining steps, always take great care to not touch any of the hot components with the glovebox gloves. Always use the tongs (J) and/or 9” long-handled tweezers (L) to move the tools and load the shot.

6. Once the metals melt, remove the upside-down 150 mL Pyrex beaker from each crucible assembly using the tongs J, and place the beakers on the upside-down 70 x 50 Pyrex dish that is next to the hot plate. Placing the Pyrex dish and beaker on the upside-down 150 x 75 Pyrex dish prevents too rapid of a temperature change for the beakers, which can cause them to break.

7. Add additional Sn and Zn so that the crucibles are filled to ~1.5 cm from the top.

8. Replace the top 150 mL Pyrex beakers on the crucible assemblies.
Fig. A2. Assembled refining and alloying crucibles.

Fig. A3. Assembled Zn and Sn refining crucibles and Pyrex housings on hot plate. The Pyrex cooling dish is next to the hot plate on the right.
After 20 minutes, the melts will reach maximum temperature.

9. 30 minutes later, remove the top Pyrex beakers from the crucible assemblies with the tongs, and place on the upside-down 150 x 75 Pyrex dish that is next to the hot plate.

10. Using the long-handled tweezers, very slowly insert a graphite stirring rod into the Sn and Zn crucibles to agitate the melts. Take great care to not overflow or splash the molten metals from the crucibles, especially not on the glovebox gloves.

11. Replace the top Pyrex beakers onto the crucible assemblies.

12. 30 minutes later, remove the Sn crucible/Pyrex beakers assembly from the hot plate using the J with L as a bottom support and place on the upside-down 150 x 75 Pyrex dish next to the hot plate.

13. After 10 minutes place the Sn crucible/Pyrex beakers assembly on the metal glovebox surface for further cooling.

14. 30 minutes later, stir the Zn melt again using the procedure of Step 10.

15. After an additional 30 minutes, remove the Zn crucible/Pyrex assembly from the hot plate using the J with L as a bottom support and place on the upside-down 150 x 75 Pyrex dish next to the hot plate.

16. After 10 minutes place the Zn crucible/Pyrex assembly on the metal glovebox surface for further cooling.
The Sn refining crucible was at maximum temperature on the hot plate for 1 hour plus the time it took to stir the melt once. The Zn refining crucible was at maximum temperature on the hot plate for 2 hours plus the time it took to stir the melt twice.

1.5 hours after removing the refining crucibles from the hot plate and placing on the metal glovebox surface, the metals will reach room temperature.

**Alloying the growth charge**

1. 1 hour after Step 16 of the refining procedure, disassemble the Sn-refining assembly, separate B from C, and cut off a piece of Sn using the wire clippers (M) and L. Place the Sn in a clean plastic bag.

2. Weigh the Sn on a scale that is inside the glovebox. The target mass is 1.45 grams.

3. Place the alloying crucible bottom (G) inside the 70 x 50 Pyrex dish that is on the hot plate, and place the alloying crucible (H) on top of G.

4. Drop the Sn piece into G and H. Cover with the alloying crucible top (I), cover G, H and I with the 150 mL beaker, and turn the hot plate on to maximum power.

5. After 30 minutes, remove the 150 mL beaker, using J and place the on the upside-down 150 x 75 Pyrex dish next to the hot plate.
6. Dissemble the Zn-refining assembly, separate E from D, and cut off a piece of 
Zn using the wire clippers (M) and L. The length of the Zn-piece should be 
approximately 0.75 cm.

7. Pick up I using J.

8. Immediately drop the Zn piece into the molten Sn melt, using L, and replace I 
on the alloying crucible. Re-cover with the 150 mL beaker.

9. After 30 minutes, remove the top, upside down 150 mL beaker and agitate 
the melt by picking up and dropping I using J. Re-cover with the 150 mL 
beaker.

10. After an additional 30 minutes, remove the alloy crucible/Pyrex beakers 
assembly from the hot plate using the tongs with the long-handled tweezers 
as a bottom support and place on the upside-down 150 x 75 Pyrex dish next 
to the hot plate.

11. After 10 minutes place the Zn crucible/Pyrex beakers assembly on the metal 
glovebox surface for further cooling.

12. Let cool for a minimum of 6 hours.

13. Dissemble the alloying crucible and place the alloy growth charge in a clean 
plastic bag.

14. Measure the final mass of the alloy growth charge to determine the 
constituent mass percentages. The best growth result was achieved with 
12.5% Zn, by mass.
15. Put the growth charge in a plastic bag and place the bag in the SPI SamplePreserver capsule for immediate transport from the glovebox to the growth chamber.
Appendix B

Procedure for the growth experiments

Prior to the alloy charge preparation steps described in Appendix A, the growth chamber is cleaned and prepared for the growth experiment: The quartz tube, boron nitride (BN) crucible, BN insulating surfaces of the crucible apparatus, and chamber windows are cleaned with HCl:H₂O 1:10, rinsed with deionized water, and dried with Kimwipes or compressed N₂.

Loading the growth charge

1) Secure the crucible apparatus in place, connect the thermocouple and heater current wires, check for short/open circuits, check that the resistance of the heater and current lead set up is correct.

2) Momentarily turn the current on to 10 amps to check the temperature responsiveness of the heater.

3) Close all gas line valves.

4) Shut the vacuum system and turn on the roughing/backing pump and turbo pump. Check that the system base pressure is reached.

5) Turn off the turbo pump.

6) Isolate the roughing/backing pump and turn it off. Vent the roughing/backing pump. Let the turbo pump slow down under vacuum.

Always allow at least 10 minutes for the turbo to slow down under vacuum.

7) Vent the system with N₂ process gas.

8) Prior to loading the growth charge into the vacuum chamber, turn on the roughing/backing pump but keep it isolated from the vacuum chamber.

9) Leaving the N₂ venting gas flowing, open the system and quickly load the crucible with the prepared alloy growth charge using 9” long-handled tweezers. Minimize the exposure time of the growth charge to atmosphere.

10) Close the vacuum chamber, shut off the venting gas flow, and pump the system with the roughing/backing pump.
11) Turn on the turbo pump.

12) Repeat the circuit checks of Steps 1) and 2).

**Preparing the gas lines**

1) Set the H\textsubscript{2} and N\textsubscript{2} mass flow controllers (MFCs) to 40 sccm.

2) With the gas sources valves (those nearest the gas sources) closed, evacuate the gas lines.

3) After the gas lines are evacuated – when the MFCs read \~1-2 sccm – shut off the H\textsubscript{2} and N\textsubscript{2} inlet valves (those nearest to the growth chamber) and turn off the MFCs.

4) *Slowly* open the gas source valves, refilling the gas lines.

5) Open the H\textsubscript{2} and N\textsubscript{2} inlet valves, and begin a 40 sccm flow from each line.

6) Let the gases flow for 30 minutes to purge the lines.

7) Set the H\textsubscript{2} and N\textsubscript{2} flow rates to 5 sccm and 40 sccm, respectively, – the growth flow rates – and adjust the gate valve so that the pressure is \~25 mTorr.

**Cleaning the growth melt and starting the growth**

1) Set the H\textsubscript{2} flow to 40 sccm and the N\textsubscript{2} flow to 0.

2) Turn on the plasma, increase the forward power (FP) to 240 W while adjusting the reflected power (RP) to less than 1% of the FP.
3) Turn on the current source and adjust the current so the melt temperature is 250 °C.

4) Clean the melt of oxides under the H₂ plasma for approximately 6 hours.

The time it takes to clean the melt depends on the particular growth melt and varies for each experiment. The melt surface will not get entirely clean of the oxides. The goal is to achieve a clean ‘oculus-shaped’ area at the top of the melt – an approximately 4 mm diameter, specular, metallic metal surface on which the quartz tube is clearly reflected. Sometimes, after 6 hours, the melt will still contain a uniform oxide shell. If this is the case, rapidly, with the current set to 95 amps, and briefly increase the temperature to ~400 °C to break up the shell with the convective flow of the melt. It is advisable to not do this more than two times because it depletes the melt of Zn. If the oxide shell remains after the temperature ramp, it is advisable to continue cleaning at 250 °C for an additional couple hours until a clean surface is achieved. If this does not occur in a reasonable amount of time, growth can begin on the still oxide-coated surface, however this is non-optimal.

5) Once the melt is clean, increase the H₂ flow to 80 sccm and set the N₂ flow to 40 sccm, while adjusting the plasma RP.

Growth experiments have demonstrated that nitride growth will not occur with the H₂ flow rate set high – approximately two times the N₂ flow rate.
6) Rapidly – set the current to 95 amps – increase the melt temperature to 10 degrees minus the target growth temperature. Adjust the current to settle near the target growth temperature.

The large H\textsubscript{2} component of the gas flow stabilizes the remaining oxide layer so that it does not break up and migrate to the clean melt surface. The higher pressure at this high gas flow rate also decreases Zn evaporation loss. The N\textsubscript{2} component of the plasma may also decreases Zn evaporation loss by coordinating with the Zn.

7) Decrease the H\textsubscript{2} flow rate to 5 sccm, while adjusting the plasma RP and current – to account for the pressure-dependent melt temperature change.

8) Adjust the gate valve so that the pressure is 30 mTorr.

9) Grow for the desired amount of time while maintaining the temperature, pressure and RP settings.

**Ending the experiment**

1) Shut off the current

2) Let the temperature decrease to around 100 °C.

3) In rapid succession, turn off the N\textsubscript{2} flow, H\textsubscript{2} flow, and plasma FP.

4) Let the growth charge cool to room temperature.

5) Turn off the vacuum pumps, vent the system, and remove the crucible apparatus.
Appendix C

In this appendix, we provide a catalog of the various types of isolated cation exchange defects and a preliminary catalog of the defect complexes composed of two-cation exchange defects.

Figure C1 shows the six types of isolated exchange defects possible on the Pna2₁ heterovalent ternary lattice. These defects can be seen as excitations on the underlying ground-state Pna2₁ lattice.

The six types of isolated defects pictured in Fig. C1 can be divided into two categories: those that exchange within the a b plane (Fig. C1 (1-4)), and those that have a c axis component in their exchange (Fig. C1 (5-6)).

In the remainder of Appendix C we will catalog the complexes of two-cation exchange defects that can form from the two categories of isolated defects. We will use the isolated defects shown in Fig. C1.4 and Fig. C1.6.
Fig. C1. The six types of isolated cation exchange defects in the Pna2₁ lattice. Large spheres are the cations, small spheres are the anions. The large discs marked by Xs are cations displaced from their ground state locations.
There are 102 possible two-cation exchange defects. 66 of these defect complexes generate a total of 5 acceptor-donor pairs, 33 complexes generate 6 acceptor-donor pairs, and 3 complexes generate 4 acceptor-donor pairs. These complexes are catalogued in Table C1.
Table C1. Catalog of two exchange defects of the type shown in Fig. C2. The first two columns label the positions of the second exchange defect. The third column gives the number of acceptor octet-rule violations in the tetrahedra surrounding Defect 1. Columns 4 through 6 are similar to column 3. Column 7 gives the total count of acceptor-donor (A-D) pairs generated by the two cation exchange defect complex.

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Like the atomic arrangement shown in Fig. C2, there are 102 possible two cation exchange defect complexes that can be generated from Fig. C3. 66 of these defect complexes generate a total of 5 acceptor-donor pairs, 33 complexes generate 6 acceptor-donor pairs, and 3 complexes generate 4 acceptor-donor pairs. These complexes are catalogued in Table C2.
Table C2. Catalog of two exchange defects of the type shown in Fig. C3. The first two columns label the positions of the second exchange defect. The third column gives the number of acceptor octet-rule violations in the tetrahedra surrounding Defect 1. Columns 4 through 6 are similar to column 3. Column 7 gives the total count of acceptor-donor (A-D) pairs generated by the two cation exchange defect complex.

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