MgSnN$_2$: A New Eco-Friendly Wide Band Gap Semiconductor

Krystal R. York

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MgSnN$_2$: A NEW ECO-FRIENDLY WIDE BAND GAP SEMICONDUCTOR

by

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A thesis submitted to the Graduate College in partial fulfillment of the requirements for the degree of Master of Science Electrical and Computer Engineering Western Michigan University June 2018

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MgSnN$_2$: A NEW ECO-FRIENDLY WIDE BAND GAP SEMICONDUCTOR

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Western Michigan University, 2018

Materials having a wide band gap (above 2 eV) can provide new alternatives for existing light-emitting diodes (LEDs) and other opto-electronic devices. Currently, many such devices are comprised of low-earth-abundant elements, such as gallium and indium, which are harmful to the environment to extract and difficult to recycle. Alternatively, MgSnN$_2$ is an unexplored material comprised of earth abundant elements which benefit from a mature recycling infrastructure. This material has a predicted band gap of 3.43 eV, indicating that it could be a viable substitute for GaN (band gap of 3.4 eV), which is commonly used in LEDs and other device applications.

In this work, samples of MgSnN$_2$ were grown via plasma-assisted molecular beam epitaxy, a high-precision process for depositing thin-film, crystalline materials on substrates. Since this material had not previously been experimentally realized, the process and parameters used to achieve high quality films were studied in depth. Several techniques were employed to analyze these samples, including reflection high-energy electron diffraction and x-ray diffraction. These techniques were used to determine the lattice constants, band gap, and crystal symmetry of a range of samples which were compared to the theoretical predictions of Jaroenjittichai and Lambrecht.
ACKNOWLEDGMENTS

There are several people that I would like to thank who have helped make this project possible and supported me throughout my Masters degree. First, I would like to thank my mentor and committee chair, Dr. Steven M. Durbin, without whose guidance and support this project would not have been possible. I am extremely grateful for all of your feedback, knowledge, and kindness that continues to encourage me throughout my education. I would also like to thank my committee members Dr. Damon Miller and Dr. Asghar Kayani for their time and support.

I would also like to express my gratitude towards my collaborators this project: Dr. Patrice Miska who performed the Raman spectroscopy measurements on our samples; Dr. Roger Reeves who performed the absorption edge measurements; Dr. Nancy Senabulya and Dr. Roy Clarke for helping us get access to Argonne National Laboratory and for helping us obtain the the X-ray diffraction measurements; Dr. Emmanouil Kioupakis, Ms. Christina Jones, Mr. Logan Williams, and Mr. James Mathis for additional support throughout this project. Furthermore, I would like to thank Robert Makin who was there with me during every film growth, extrapolated the band gap measurements from the absorption edge data, and answered several questions I had throughout this project.

Finally, I would like to thank my loving family and friends. Without their endless support and encouragement I would not be where I am today. Thank you for always being there when I needed a hug and someone to talk to.

Krystal R. York
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1 Introduction

1.1 Motivation to Find a New Wide Band Gap, Earth Abundant Element Semiconductor

Silicon remains an important semiconductor material for many electronics applications, but its low absorption coefficient reduces its competitiveness in the high efficiency solar cell arena, and its indirect band gap is a poor match for light emitting diode and solid-state lighting applications [1]. Consequently, such applications have led to the development of direct band gap compound semiconductors based on gallium and indium. However, these two metals are not especially abundant, are currently sourced primarily through mining, and future supply is uncertain [2]. Alternative semiconductors based on other metals are therefore needed.

The goal of this project is to synthesize—for the first time—high quality crystalline thin films of a proposed new wide band gap semiconductor, MgSnN$_2$, via plasma-assisted molecular beam epitaxy (PAMBE), based on previous experience with the closely related narrow band gap semiconductor ZnSnN$_2$. Whereas ZnSnN$_2$ is of interest for solar cells, MgSnN$_2$ could be useful for solid state lighting and water sterilization, among other short wavelength device applications. It may also prove useful as a barrier layer in ZnSnN$_2$-based heterostructure devices. Like zinc and tin, magnesium is considered eco-friendly since it is highly recyclable [2]. MgSnN$_2$ has been identified through first principles computational efforts (a cornerstone of the Materials Genome Initiative [3]) as a potential wide gap semiconductor; however, before this research, it had not been synthesized [4]. Consequently, a plan
was developed to demonstrate a pathway to obtaining high-quality crystals of this material, and experimentally verify properties predicted by theory.

Systematic variation of process parameters has led to the realization that the lattice structure of ZnSnN\(_2\) (and closely related materials) can be controlled and switched between orthorhombic and wurtzite [5, 6]. The lattice structure has a direct effect on the band gap of the material, and process parameters also affect crystal quality through defect type, which can adversely control electronic properties important to devices. Thus, part of the project is focused on process parameters that result in the desired crystal structure, the necessary crystal quality for devices, and the fundamental optical and electronic properties of this semiconductor, as they relate to ordering of the Mg, Sn (cation) sublattice.

### 1.2 Material Sourcing

The Mineral Commodity Summary prepared by the U.S. Department of Interior is a review of the mineral industries in the United States and many other countries. This comprehensive document evaluates the production, use, cost, and recycling infrastructure, and also estimates the global reserves. The detailed report for magnesium and tin indicate that both of these metals are fairly inexpensive compared to many of the commonly used elements for compound semiconducting devices, including gallium [2]. The predicted band gap, which is the focus of the present work is a close match to that of GaN (3.4 eV), a wide band gap material commonly used in light emitting diodes (LEDs) and blue lasers [4]. Figure 1.1 displays the relative price of these elements from 2000 to 2016, clearly showing Ga being significantly more costly (per kilogram) than Mg and Sn [2]. Consequently, MgSnN\(_2\) is not only an environmentally friendly alternative to GaN, but also a cost effective one.
There are a number of motivations to put forth environmentally-friendly alternatives, such as MgSnN$_2$, to existing semiconducting materials. Semiconducting compounds are commonly used in applications such as photovoltaics, opto-electronics, and high-speed electronics. Many of the common semiconducting compounds used in devices today are made of expensive and earth-depleting elements such as gallium and indium [2, 6, 7].

Magnesium and tin demonstrate that both of these metals have a developed recycling infrastructure having thousands of tons recovered from old and new scrap [2]. When evaluating the years 2000 through 2016, magnesium had between 66,000 and 89,000 tons recovered each year, and tin had between 8,830 and 15,700 tons recovered each year from old and new scrap. This is significantly different from the statistics found on gallium which shows every year, dating back to 2000, there has not been any old scrap recovered. Although there has been some new scrap recovered by one company, this
would not be considered a maintainable source of gallium [2]. Compounds comprised of highly recyclable elements, such as magnesium and tin, could prove to be an excellent alternative for other semiconducting materials that use less eco-friendly and less abundant elements. A reliable infrastructure to acquire and recycle metals needed for modern technologies is critical.

1.3 II-IV-V$_2$ Materials

Several II-IV-V$_2$ materials (heterovalent ternary materials) have been previously studied and reported results show that they could be suitable for optoelectronic applications [8–12]. Their structure is notably based on the anion (group V element), as the phosphide and arsenide materials exhibit a chalcopyrite structure and the nitride materials exhibit an orthorhombic structure in equilibrium. They are closely related to the extensively explored III-V materials, with the group III elements replaced with alternating group II and group IV elements (for example, ZnSnAs$_2$ is an analog to GaAs). III-V materials currently dominate much of the optoelectronic technologies,

![Figure 1.2: Band gap and lattice constant comparison between the II-IV-N$_2$ and the related III-N materials. Figure adapted from [10].](image-url)
but II-IV-V\textsubscript{2} materials have been shown to cover essentially the same range of band gaps and have other unique characteristics (Fig. 1.2). [10].

Photovoltaic device applications are a prominent focus when it comes to II-IV-V\textsubscript{2} materials. Most significant are ZnSnN\textsubscript{2}, ZnSnP\textsubscript{2}, and ZnGeAs\textsubscript{2} materials, since the ideal band gap for a terrestrial single junction solar cell is around 1.4 eV, and these materials have band gaps between 1.0 eV and 1.9 eV. The primary challenges for these materials include the high zinc flux necessary to grow high quality thin films, the volatility of zinc, and the formation of competing phases that originate from the complexity of the ternary phase space. Despite such issues, these materials have been successfully realized using various techniques [6, 10, 13, 14]. Photovoltaic (PV) device fabrication has also been reported for II-IV-V\textsubscript{2} materials. A PV device based on thin film ZnGeAs\textsubscript{2} and also a single crystal flux-grown wafer ZnSnP\textsubscript{2} have reported efficiency ratings below 0.1%, whereas a thin-film heterojunction ZnSnN\textsubscript{2} solar cell has a reported efficiency rating of about 0.37% [10]. Although there are significant challenges to overcome before these become reliable PV devices, early results show the capability of the materials to reach device quality.

Alloying is another capability that has been demonstrated in some II-IV-V\textsubscript{2} materials to tune parameters. ZnSn\textsubscript{x}Ge\textsubscript{1-x}N\textsubscript{2} alloys in particular have been the focus of several detailed studies [15, 16]. This alloy has been reported to have a band gap anywhere between approximately 1.5 eV and 3.6 eV, which is the ideal range for several applications such as solar cells and LEDs. Alloys still need to overcome problems with transport properties and band offsets as well as typical expensive, adverse effects such as clustering and miscibility gaps, before quality devices can be achieved [10, 15, 16]. Consequently, while alloys allow tuning, other considerations may make them less attractive.
One of the most significant advantages of the heterovalent ternary nitrides over the III-nitrides is the possibility of varying degrees of cation sublattice ordering. Another advantage comes from point defect physics, which opens up new possibilities for doping and can control electronic properties important to devices. The ability to dope a material using p-type doping has been problematic for III-N materials. Ternary nitrides, however, have been proven to be able to be doped p-type, at least in the case of ZnGeN$_2$ [17]. The capability for semiconductors to be doped both p-type and n-type is essential in making high-efficiency opto-electronic devices [4, 17]. The hope is that this and other advantageous properties that have been discovered in some II-IV-V$_2$ materials can be identified and exploited in MgSnN$_2$.

1.4 MgIVN$_2$ Family

There have been preliminary tests to estimate the lattice parameters, unit cell, and band structures of some members of the MgIVN$_2$ family. These compounds have a $\beta$-NaFeO$_2$ crystal structure that is comparable to the III-N wurtzite structure, and belong to the Pna2$_1$ (number 33) space group. Both MgSiN$_2$ and MgGeN$_2$ have been both theoretically and experimentally explored with the calculated values closely matching the experimental values. The first report of heterovalent ternary II-IV-V$_2$ compounds were made by Goodman in 1956 [18, 19], which predated the first report of GaN by 15 years [20]. Consequently, the nitride materials are more contemporary and hence less understood. In 2016, Jaroenjittichai and Lambrecht published first principle calculations of MgSnN$_2$, which until now has not been synthesized [4]. By replacing zinc with magnesium, it increases the band gap range of ternary nitrides into the UV region allowing these nitrides to extend opto-electronic properties [4].

The direct band gap (3.43 eV) and lattice constants ($a = 6.905$ Å, $b = 5.932$ Å, and $c = 5.499$ Å) of MgSnN$_2$ were estimated using gradient approximation (GGA),
however these measurements have not been experimentally confirmed [4]. This predicted band gap is within the UV region indicating this semiconductor material would exhibit opto-electrical properties. This present work looks to provide the first experimentally measured band gaps and lattice constants of MgSnN$_2$, thus being able to compare to the values found in the work of Jaroenjittichai and Lambrecht.

The properties of MgSiN$_2$ have been investigated both theoretically and experimentally. This material has an indirect band gap of 5.84 eV as well as a direct band gap of 6.28 eV that is closely related to the band gap of the widely used material AlN (6.2 eV). AlN is used for various applications such as opto-electronics, sensors, and electronic substrates when there is a need for high thermal conductivity. [4]. Ceramic samples of MgSiN$_2$ have been investigated as a possible alternative for substrates because of its advantageous thermal, mechanical, and luminescence properties [21–23].

MgGeN$_2$ has been explored alongside MgSiN$_2$ in several studies. The direct band gap of MgGeN$_2$ has been theoretically calculated and experimentally measured to be about 5.14 eV, which is below the band gap of AlN and higher than the band gap of GaN (3.4 eV) [4]. Both MgGeN$_2$ and MgSiN$_2$ have had experimental studies done on their phonon properties, heat conductivity, and heat capacity [21] as well as their lattice dynamics and thermal expansion [24]. The Mg-IV-N$_2$ materials are all being considered possible alternatives for deep UV-LEDs and other wide band gap devices [4,21,24].

1.5 Overview of Thesis

The organization of the remaining chapters of this thesis is as follows.
Chapter 2 provides an overview of the equipment used throughout the project as well as the techniques employed. Much of this chapter is devoted to explaining the techniques of molecular beam epitaxy (MBE) and the comparison in-situ characterization technique known as reflection high energy electron diffraction (RHEED). Other equipment available to characterize the films grown include the quartz crystal microbalance (QCM), Rutherford backscattering spectrometry (RBS), and x-ray diffraction (XRD).

Chapter 3 discusses the growth experiments leading up to achieving single crystal growth of MgSnN$_2$. It explores the parameters that were used to grow each film and explains why certain parameters were altered between experiments. Additionally, it investigates the results of the preliminary polycrystalline films. This chapter concludes with an explanation of the parameters for the single crystal films that were grown, and what were the most important changes made to achieve those results.

Chapter 4 displays all of the key results for the single crystal films. These results include RHEED, RBS, XRD, lattice parameters, and transmission spectroscopy. Conclusions based on these results and the parameters that correlate with the given single crystal film, including the effects of cation sublattice ordering, are provided.

Finally, Chapter 5 summarizes the findings and presents conclusions. Furthermore, this chapter outlines future work that could stem from this project, including logical next steps.


2 Equipment

2.1 Molecular Beam Epitaxy

There are several techniques used to fabricate thin-film semiconductor materials, such as evaporative methods, glow-discharge processes, gas-phase chemical processes, and liquid-phase chemical techniques [25]. In this thesis, an evaporation process called molecular beam epitaxy (MBE) was used to grow the films. This is a high-precision process dating back to 1968 when it was first used at Bell Telephone Laboratories and subsequently patented by J. R. Arthur [26]. It involves vapor deposition of elements

Figure 2.1: The Perkin-Elmer 430 MBE system used to grow the MgSnN$_2$ films. The chamber is mounted to the left and the ultra-high vacuum transfer tube extends to the right.
in an ultra-high vacuum (UHV) environment that reaches very low pressures–on the order of $10^{-10}$ torr. This enables the growth of high-quality single-crystal samples (includes metastable phases) one atomic layer at a time. A heated crystalline substrate is used as a template for a single crystal film that can measure between one atomic layer and approximately 1 micron thick. Plasma-assisted MBE (PAMBE) is a nonequilibrium (kinetic) growth process based on thermal evaporation aided by a plasma (in this case, a nitrogen plasma) [27–29]. The system employed to grow MgSnN$_2$ is pictured in Fig. 2.1.

Each type of source material (e.g. Mg, Zn, or Sn) is put in separate evaporation cells called effusion cells (Fig. 2.2). These cells are heated to the temperature needed via proportional integral derivative controllers to reach the desired flux of the constituent elements or dopants in the effusions cells with an accuracy within 1%. Flux is described as the rate at which the elements are deposited on the substrate, and is typically measured in atoms/(cm$^2$·s). The flux of the elements along with the tempera-

![Figure 2.2: Schematic of the MBE chamber. The sample block is shown in the growth position. The green rectangle on the sample block represents the substrate, whereas the other colors each represent a different element being deposited on the substrate to form the thin-film semiconductor material.](image)
ture of the substrate determine the growth rate of the film. There are pneumatically-actuated metal shutters over the effusion cells to control when the constituents will be deposited, thus controlling the growth timing and composition [27].

The growth chamber, as illustrated in Fig. 2.2, is where the interaction between the molecular or atomic beams on the heated substrate occurs. The sample block enters the chamber manually from the transfer tube. This entire system is a controlled environment that maintains a low pressure and keeps out contaminants while having an easy way to load substrates in and take samples out. This transfer is done through a 6-sample cassette based load lock. This system allows us to grow several films without having to bring the system up to atmospheric pressure.

2.2 Reflection High-Energy Electron Diffraction

Reflection high-energy electron diffraction (RHEED) is an experimental technique used to observe the growth of material in-situ. It is a powerful analytical tool used to examine the structure of the crystal surface at atomic levels. RHEED images are captured during growth to gather information about the material such as the lattice parameters, growth rate, crystal quality, whether it is disordered or ordered, whether it is rough or smooth, and much more. This technique is commonly paired with MBE due to ultra-high vacuum environment. At higher pressures it is difficult or impossible to obtain RHEED images on the phosphor screen since the electrons would scatter off the high density of atoms in the chamber [30–32].
Figure 2.3: A schematic of the experimental set-up of the RHEED system. The electron gun focuses an electron beam at the sample surface at a small angle of just a few degrees. This beam will scatter in a distinct diffraction pattern at a phosphorescent screen where the pattern is recorded by a CCD camera.

A typical RHEED system, as shown in Fig. 2.3, involves a focused electron source, phosphor screen, and a clean surface to hold the sample. The system used in the WMU MBE lab is a 20 kV Staib instruments electron source. The electron source aims an incident beam of electrons at high energies (accelerated to between 10 kV and 20 kV) directed at a low angle \( \theta \) (around 2°) to the surface of the sample. This glancing angle is varied by both electrostatic deflection and sample motion. The high electron energy allow the majority of scattering to be in the forward direction and also enables dynamical analysis. Additionally, higher energies allow the pattern to be reduced by a factor proportional to the square root of the energy to allow for some gain to the amount of Laue zones that can be detected. The incident beam only has a small penetration depth from the interaction between the incident electrons and the atoms, meaning that the RHEED system is able to very precisely observe the first few layers of the sample. The diffracted beams, incident on a phosphor screen, are recorded on a charge-coupled device (CCD) camera. A kSA capture and analysis package (which
includes the CCD camera) is employed to analyze the RHEED images [30–32].

A three-dimensional real space volume has a corresponding three-dimensional reciprocal space. However, RHEED is a surface sensitive measurement technique where the high energy electron beam only probes the first few atomic layers of the material. Thus, the beam diffracts through a two-dimensional surface lattice and not through the three-dimensional bulk lattice of the crystal. The RHEED pattern can be viewed as a Fourier transform of real space to reciprocal space and is characterized by what is known as the Ewald sphere (seen in Fig. 2.4a). The crystal is located at the center of the sphere where the radius is equal to the wavevector of an electron

\[ \mathbf{k} = \frac{2\pi}{\lambda} \]  

(2.1)

where \( \lambda \) is the wavelength of the incoming electron beam. Wherever the sphere intersects a reciprocal lattice rod (as opposed to a reciprocal lattice point, since we are considering a two-dimensional surface in real space), it results in a scattering maxima, and a corresponding pattern is evident on the detector. The periodic pattern satisfies the Laue condition

\[ \mathbf{G}(hk) = \mathbf{k}_{out} - \mathbf{k}_{in} \]  

(2.2)

where \( \mathbf{G} \) is the reciprocal lattice vector, \( \mathbf{k}_{in} \) is the incident wavevector, and \( \mathbf{k}_{out} \) is the outgoing wavevector. Laue rings exist where the Laue conditions are met and constructive interference can occur, forming a diffraction pattern [30,32,33]. An image of a typical single crystal RHEED pattern from a (111) YSZ substrate is shown in Fig. 2.5. The desire is that when growth begins, the thin, straight streaks will remain, indicating that the material is a single crystal.
Figure 2.4: (a) Visualization of an Ewald sphere with radius $|\mathbf{k}|$. This is an aid to help determine the pattern that will be shown on the RHEED screen. (b) Streaks form perpendicular to the shadow edge. The shadow edge exists because the incident beam and other diffracted beams cannot travel through the substrate. The streaks (corresponding to diffraction rods) are labeled $(00)$, $(10)$, $(20)$, $(\bar{1}0)$, and $(\bar{2}0)$ by their reciprocal lattice vector $G(hk)$ above the shadow edge. Figure adapted from [34].

Figure 2.5: Example RHEED image for (111) yttria-stabilized zirconia (YSZ) substrate. The separations between the streaks on the RHEED screen are inversely proportional to the lattice spacing, meaning that for larger crystal lattices the streaks will appear closer together and more streaks will appear on the phosphor screen. Kikuchi features (diagonal features) are seen here due to inelastically scattered electrons and second order diffraction, and are an indication of a high-quality crystal structure.
A polycrystalline material has imperfections creating separate crystalline domains within the material with no preferred orientations. Polycrystalline films will lead to diffraction maxima around the Laue ring, creating arc shapes known as Debye-Scherrer rings. The diffraction maxima originate from the distribution of the lattice rods on the Ewald sphere (Fig. 2.6). The RHEED image will demonstrate the Debye-Scherrer ring pattern as seen in Fig. 2.7 [32, 33]. If there are slightly more ordered materials that have a preferred orientation along the growth direction only, the RHEED pattern will instead only demonstrate partial arcs [35].

**Figure 2.6:** (a) Like the single crystal films, the Ewald sphere is a geometric construction used as a visual aid to determine how the diffraction pattern will look like on the RHEED screen. (b) The shadowing edge exists because the incident beam and other diffracted beams cannot travel through the substrate. Spherical shells will intersect the Ewald sphere forming a diffraction pattern of continuous rings. Figure adapted from [34].
Without in-situ techniques such as RHEED, thin film growth has to be analyzed after the growth process with techniques such as x-ray diffraction (XRD), scanning electron microscopy (SEM), and scanning tunneling microscopy (STM). Thus RHEED has a significant advantage over other analysis techniques since it is performed real-time, in-situ, thus preserving the surface [32]. By comparing RHEED images to XRD results (typically taken after many samples are made since we use facilities at Argonne National Laboratory for XRD), it has been proven that RHEED can be used directly to determine whether a film is growing with a high or low degree of cation ordering. Consequently, we can use RHEED during crystal growth to study the effect of processing parameters on not only crystal quality and lattice parameters, but cation ordering as well.
2.3 X-Ray Diffraction

X-ray diffraction (XRD) is a commonly employed technique used to determine various parameters of thin film materials. XRD is much like any other diffraction technique in which a beam is aimed at a material and produces an interference pattern based on the lattice periodicity. In this analysis technique, a beam is aimed at a sample with some crystalline structure and the diffraction pattern produced can give information about the lattice parameters and overall crystal structure [36,37].

A common XRD analysis technique is the $\theta$-$2\theta$ scan. This scan involves a stationary sample, an x-ray source directed at the sample at some incident angle $\theta$, and a detector set up at a corresponding $2\theta$. A $\theta$-$2\theta$ scan records the diffraction intensity over a range of $\theta$ values. Several peaks will emerge each representing diffraction from different crystallographic planes. The final $\theta$-$2\theta$ plot obtained is then compared to a standard spectrum in order to determine the crystal structure of the material being examined [36,37].

A pole figure is another analysis tool ordinarily obtained with XRD. To acquire this diagram, the diffraction angle ($2\theta$) is fixed and the intensity of the diffraction is determined by altering the tilt angle ($\alpha$) and the rotational angle ($\beta$). The intensity data are then plotted as a function of these two angles. Unlike a $\theta$-$2\theta$ scan, the sample is rocked while there is a fixed x-ray source, which will produce a fixed scattering vector $\mathbf{k}$ (also referred to as the wavevector). The end of the scattering vector will form a sphere; however, it is easier to visualize the diffracted intensity variation in two-dimensions as a stereoscopic projection (Fig. 2.8) [38].
Figure 2.8: Visualization of how to conduct a rocking curve scan where the x-ray source remains fixed (which makes the scattering vector \( k \) fixed) as the sample is rotating. The diffracted intensities are then seen in two-dimensions as a stereoscopic projection, which is referred to as a pole plot. Intensity data is plotted as function of the tilt angle \( \alpha \) and the rotational angle \( \beta \). Figure adapted from [38].

Bragg’s law

\[
n\lambda = 2d\sin(\theta)
\]

(2.3)
describes the parameters at which constructive interference will occur during the XRD scans therefore creating diffraction maxima, where \( \lambda \) is the wavelength of the incident beam, \( n \) is the order, \( d \) is the lattice spacing, and \( \theta \) is the scattering angle. When two waves have the same wavelength and direction, their phase difference determines if they cancel each other or diffract. Constructive interference occurs when the waves have a phase difference of \( n\lambda \), also known as the waves being in phase [36, 37].

The XRD results in this thesis (\( \theta-2\theta \) plots and pole figures) were obtained at Argonne National Labs with the help of collaborators Dr. Nancy Senabulya and Prof. Roy Clarke. At this facility, the Advanced Photon Source, Beamline 33-BM-C: Multi-Purpose General Scattering was used as pictured in Fig. 2.9. From these measurements
different characteristics of the thin-film materials such as the crystal structure, the orientation, lattice parameters, and the shape and internal stress of individual crystalline regions were determined.

Figure 2.9: The XRD machine at Argonne National Labs that was used to take XRD measurements on the MgSnN$_2$ films.
2.4 Flux Measurements

An effusion cell, also known as a Knudsen cell, is a thermal effusion evaporator and holds the constituents used to grow the thin-film material. They are normally used in molecular beam epitaxy because of how easy it is to regulate the temperature of the evaporating materials while they are inside the low-pressure effusion cell. The cell measures the volume flow rate and the vapor pressure by measuring the vapor that has effused through the tube and determining the amount of mass that has been lost. This is accomplished by measuring the collisions in this tube and calculating the mean free path \[\lambda = \frac{RT}{\sqrt{2\pi d^2 N_A P}}\] (2.4).

The Knudsen equation

\[q = \frac{1}{6} \sqrt{2\pi \Delta P} \frac{d^3}{l \sqrt{\rho_1}}\] (2.5)

is thus needed to describe the effusion of a gas from a containing cylinder in free molecular flow at low background pressure, where \(q\) is the volume flow rate, \(\Delta P\) is the pressure drop over the length of the tube, \(\rho_1\) is the ratio of the density to pressure, \(d\) is the diameter of the tube, and \(l\) is the length of the tube [39]. To find the pressure drop over the length of the tube, the vapor pressure equation
\[ \log(P) = A + \frac{B}{T} + C \log(T) + \frac{D}{T^3} \] 

(2.6)

is used, where \( A, B, C, \) and \( D \) are all constants depending on which element is being examined and if the element is either in the solid or liquid state of matter, \( T \) is the temperature in Kelvin, and \( P \) is pressure in atmospheres [41].

The Knudsen equation is based on the assumption that the rate at which the molecules are flowing through the tube is equal to the rate where the molecules would hit that small area of the wall if the tube was not open. For this assumption to hold true, the radius of the hole must be significantly smaller than the mean free path. Because of the vacuum in place, there will be a low vapor pressure (on the order of \( 10^{-10} \) torr) inside the MBE machine creating a long enough mean free path to allow for the Knudsen equation to be accurate [27, 29, 39]. Initial measurements can be made using equations 2.4-2.6 to determine the desired temperature that will provide the desired flux of each element used to grow a material.

There are several ways to measure flux in an MBE environment, but for this work a quartz crystal microbalance (QCM) was employed. As mass is deposited on a quartz crystal that is lowered into growth position, the oscillation frequency of the quartz crystal changes proportional to the amount of mass deposited on the quartz crystal. The change in frequency is given by the Sauerbrey equation

\[ \Delta f = -C_f \Delta m \] 

(2.7)

where \( \Delta f \) is a small change in oscillation frequency measured over a predetermined time period, \( \Delta m \) is the change in mass per unit area of the crystal, and \( C_f \) is the sensitivity factor for the crystal. The change in mass is the amount of deposited mass accumulated on the quartz crystal in a determined time interval. \( C_f \) is a property
the QCM and given by

\[ C_f = \frac{2f_0^2}{A(\sqrt{\rho_q\mu_q})} \]  \hspace{1cm} (2.8)

where \( f_0 \) is the resonant frequency of the unloaded crystal, \( \rho_q \) is the density of the quartz, \( \mu_q \) is the shear modulus of the quartz, and \( A \) is the active crystal area, described by the area between the electrodes. The density of quartz is a constant, equal to 2.648 g·cm\(^{-3}\). The shear modulus of quartz is also a constant, equal to 2.947 \times 10^{11} \text{ g·cm}^{-1}\cdot\text{s}^{-2} [42–44].

The Sauerbrey equation is used to determine the amount of mass deposited on the crystal for a fixed change in frequency. As shown in Eq. 2.7, the mass charge per unit area at the QCM electrode surface is related to the change in oscillation frequency of the crystal. In the current MBE system, measurements are performed by lowering the crystal microbalance into the growth position. The crystal can be made to oscillate at its resonant frequency (approximately 6\times10^6 \text{ Hz in MBE}) when connected to a driving oscillator circuit. Adding mass to the crystal leads to the frequency at which the crystal vibrates being decreased. This frequency change, in conjunction with knowledge of the atomic mass, can then be used to calculate the thickness of the layer we deposited on the substrate as well as the flux of that particular element [42–44].

Once the flux measurement is taken, it can be compared to the target flux values and the temperature can be adjusted if needed. The measurements can be adjusted to better predict the temperatures needed to reach the desired flux. This is done by dividing the experimental flux measurement by the calculated value at that temperature and then multiplying all the flux measurements by this ratio. Figure 2.10 displays an example flux curve for Mg, which is used to predict what temperature is needed to produce the desired flux.
Figure 2.10: This is an adjusted flux curve for Mg with a logarithmic y-axis. If a Mg flux of \(10^{13}\) atoms/(cm\(^2\)·s) is desired, this graph shows the Mg temperature should be about 400 °C.

2.5 Nitrogen Plasma Source

The nitrogen plasma source used to supply the active nitrogen in the MBE system is the Oxford Applied Research HD25 inductively-coupled RF plasma source equipped with a 256-hole aperture plate with electrostatic ion removal. The nitrogen pressure is measured by an ionization gauge, which is used indirectly to measure the flux. The radio frequency (RF) power of this nitrogen source is typically between 100 and 250 W, but every material in this thesis was grown at a nitrogen plasma power of 150 W. This maintains the plasma source in high brightness mode, which is the preferred mode during growth (based on the desired active species).

The nitrogen source can produce both atomic and metastable excited molecular nitrogen. The ratio of these can be controlled by two parameters: the \(\text{N}_2\) flow rate
and the RF power. In past studies, molecular nitrogen has shown to increase as the RF power and the N$_2$ flow rate increases [45]. Although the amount of atomic nitrogen also increases with RF power, flow rate does not seem to have a significant effect. A typical spectrum of the nitrogen plasma emission is shown in Fig. 2.11. The concentration of molecular and atomic nitrogen present in the plasma can be determined by examining the spectrum. The atomic nitrogen is represented by the sharp peaks whereas the molecular nitrogen is represented by the broader ones. Previous studies have concluded that molecular nitrogen tends to lead to better quality thin-film materials, therefore parameters that produce higher molecular nitrogen content were chosen in this work [5, 33, 45].

![Figure 2.11: Example of a typical nitrogen plasma emission spectrum acquired from the HD 25 plasma source. This particular emission was taken when the RF power was at 150 W, the chamber pressure was at $2.75 \times 10^{-5}$ torr, and the nitrogen flow rate was 0.625 sccm. The sharper peaks represent atomic nitrogen and the broader peaks represent molecular nitrogen. Some peaks are labeled for reference.](image-url)
2.6 Rutherford Backscattering Spectrometry

Rutherford backscattering spectrometry (RBS) is a method used to determine the atomic mass, distribution of depth, and thickness of elements in a material. It does this by scattering charged particles in a Coulomb field, which involves firing a beam of positively charged ions (He\(^{2+}\) ions are used in this work) with energies in the MeV range at a target. A linear accelerator is used to accelerate an atomic beam to these high energies. Once the ions reach the target, particles undergo elastic collisions and are deflected back (backscattering) in the direction that they came from to transfer energy to a stationary nuclear particle detector [46,47].

RBS measurements can be performed at the WMU accelerator facility, which uses a High Voltage Engineering Corporation 6-MV model EN tandem Van de Graaff type accelerator. This equipment is used to accelerate the particles to a suitable energy by means of a fixed electric field. SIMNRA software [48] is used to analyze the RBS spectrum. This software simulates the backscattering spectra for ion beam analysis as shown in Fig. 2.12. The red line in the figure displays the RBS spectrum for the elements examined. The blue line is the data fitting line to the backscattering spectra. The line is used to calibrate the data taken of the films since the samples were mounted onto copper tape. The energy per channel determined from fitting the copper spectrum is used to fit the RBS data from the sample as the exact composition is not known. This information as well as the parameters known from the RBS experimental set-up can be used to identify both the thickness and the percentage of each element in the sample.
Figure 2.12: The red line in the figure above displays the RBS spectrum for copper. The blue line is the data fitting line to the backscattering spectrum. The energy per channel from fitting the copper spectrum is used to fit to a sample when the exact composition is not known. By fitting the line, the thickness and the percentage of each element in the sample can be determined.
3 Methodology

3.1 Introduction

Since there are no reports of MgSnN\(_2\) ever being synthesized before this work, the initial parameters were based on previous reports on closely related material. Because of its similarities with ZnSnN\(_2\) and our experience with growing this material by PAMBE, the beginning parameters were chosen based on the optimal parameters to grow a ZnSnN\(_2\) film. Additionally, Jaroenjittichai and Lambrecht in 2016 reported ab-initio calculations of the lattice parameters of MgSnN\(_2\) using GGA, local density approximation (LDA), and quasiparticle-self-consistent GW (QSGW) methods, which were used to select substrates. Finally, theoretical and experimental studies on MgSiN\(_2\) and MgGeN\(_2\) proved to be useful from the perspective comparisons to ZnSnN\(_2\) [4].

3.2 Preliminary Films

Table 3.1 summarizes the parameters used on the first synthesized MgSnN\(_2\) films. Additionally, every one of these films had a nitrogen pressure of \(2.66 \times 10^{-5}\) torr and the plasma source was set to 150 W. For our first growth experiment, a Mg flux of \(10^{15}\) atoms/cm\(^2\)·s was needed. To determine the cell temperature, the flux curve was used in conjunction with preliminary measurements. A high Mg:Sn flux ratio of 75:1 was chosen because Mg has a somewhat lower vapor pressure than Zn (which is typically grown at about 100:1 Zn:Sn ratio), but it still has a much higher vapor pressure than Sn. The rest of the parameters were kept the same as employed for single crystal ZnSnN\(_2\). During growth, the RHEED streaks began to show arc-like features within 25 seconds (corresponding to a film thickness of approximately 1 nm), indicating that
the film was becoming polycrystalline. This was most likely due to insufficient Mg, therefore, the next film was grown at a higher Mg to Sn flux ratio.

To determine the adjustment needed to the Mg flux, the growth temperature of Mg was increased 35 °C (410 °C to 445 °C) to reach the desired ratio of 100:1. Once again, RHEED images illustrated that the film was forming in a polycrystalline fashion at about 50 seconds into the growth process (corresponding to a film thickness of approximately 2 nm). However, a better quality film can be seen with the final growth image shown in Fig. 3.1b. RHEED images signify better quality films when there are thin, clearer features observed. The need for a higher substrate temperature was determined after considering the Mg-Sn eutectic point. For the first two films, the substrate temperature was set to 425 °C. However, as seen in Fig. 3.2, the Mg-Sn eutectic point at this Mg:Sn ratio dictates a higher substrate temperature, on the order of 580 °C [49].

The only change between WPI-125 and WPI-126 was the increase in substrate temperature. This film growth formed a polycrystalline pattern about a minute (corresponding to a film thickness of about 1.5 nm) into growth. Since increasing the

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**Table 3.1: The PAMBE growth parameters of the four preliminary films.**

<table>
<thead>
<tr>
<th>Film #</th>
<th>Substrate Type</th>
<th>Substrate Temperature</th>
<th>Sn Flux $10^{13}$ atoms/cm$^2$·s</th>
<th>Mg Flux $10^{14}$ atoms/cm$^2$·s</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPI-124</td>
<td>YSZ(111)</td>
<td>425 °C</td>
<td>1.05</td>
<td>7.88</td>
</tr>
<tr>
<td>WPI-125</td>
<td>YSZ(111)</td>
<td>425 °C</td>
<td>1.06</td>
<td>9.50</td>
</tr>
<tr>
<td>WPI-126</td>
<td>YSZ(111)</td>
<td>580 °C</td>
<td>1.12</td>
<td>7.22</td>
</tr>
<tr>
<td>WPI-127</td>
<td>YSZ(111)</td>
<td>610 °C</td>
<td>1.20</td>
<td>8.39</td>
</tr>
</tbody>
</table>
Figure 3.1: RHEED images for the first four MgSnN\(_2\) growth experiments. These images were taken at the end of growth and all display polycrystalline growth patterns. Every film here was grown on YSZ(111). The films are identified as follows: a) WPI-124 (substrate temperature of 425 °C, Mg flux of 7.88\times10^{14}\text{atoms/cm}^2\cdot\text{s}, Sn flux of 1.05\times10^{13}\text{atoms/cm}^2\cdot\text{s}) b) WPI-125 (substrate temperature of 425 °C, Mg flux of 9.50\times10^{14}\text{atoms/cm}^2\cdot\text{s}, Sn flux of 1.06\times10^{13}\text{atoms/cm}^2\cdot\text{s}) c) WPI-126 (substrate temperature of 580 °C, Mg flux of 7.22\times10^{14}\text{atoms/cm}^2\cdot\text{s}, Sn flux of 1.12\times10^{13}\text{atoms/cm}^2\cdot\text{s}) and d) WPI-127 (substrate temperature of 610 °C, Mg flux of 8.39\times10^{14}\text{atoms/cm}^2\cdot\text{s}, Sn flux of 1.20\times10^{13}\text{atoms/cm}^2\cdot\text{s}).
substrate temperature improved the quality of the film the next film growth consisted of further increasing the substrate temperature to 610°C. This rise in temperature may be needed to reach the Mg-Sn eutectic point.

Figure 3.2: Binary phase diagram of Mg-Sn indicating the eutectic point. Below the line the elements are solid and above the line the elements melt to the liquid phase. The left side of the figure is when the material is Mg rich. Since MgSnN\(_2\) requires a high Mg:Sn ratio, the highlighted section of the graph is the important part for this research. Figure adopted from [49].

As a result of the increased Mg flux, there was some Mg “blow by” before growth began, meaning some Mg was able to reach the substrate before opening the shutters. This caused a film to begin growth before the Sn or nitrogen was introduced. Although the Mg:Sn flux ration was improved, initial RHEED images displayed polycrystalline streaks within one minute of growth. At this point, it was determined that the most likely reason for all of these films becoming polycrystalline was the significant difference between the predicted lattice parameters of MgSnN\(_2\) and the substrate YSZ(111).
3.3 Crystalline Growth of MgSnN$_2$

Lattice mismatch occurs when the lattice structure and lattice spacing do not match between the epitaxially deposited film and the substrate. The result in significant cases is often the formation of interfacial defects which can degrade the crystalline quality as well as electronic properties. To calculate the lattice mismatch between the substrate and the film the in-plane lattice constants

$$\delta = \left| \frac{a_{\text{film}} - a_{\text{sub}}}{a_{\text{sub}}} \right|$$ (3.1)

are compared, where $\delta$ is the lattice mismatch, $a_{\text{film}}$ is the lattice constant of the film, and $a_{\text{sub}}$ is the lattice constant for the substrate. Traditionally, a mismatch of about 1% was considered significant [50, 51], although the InGaN family saw this benchmark increase to about 10.6% as the dislocation network has a tendency to self-ameliorate and surprisingly is not important in terms of device performance [52, 53].

The original substrate for the first four films was YSZ(111). This crystal has a cubic structure with a lattice constant of about $a = 5.145\,\text{Å}$. However, the (111) plane is the hexagonal surface of the unit cell. Thus, the surface has axes $a_s$, $b_s$, and $c_s$ where $a_s = b_s = \frac{\sqrt{2}}{2}a$ and $c_s = \sqrt{3}a$, so that the surface cell parameters for YSZ(111) are $a_s = b_s = 3.638\,\text{Å}$ and $c_s = 8.911\,\text{Å}$ [54]. The theoretical lattice constants for orthorhombic MgSnN$_2$ are $a = 5.9\,\text{Å}$, $b = 6.9\,\text{Å}$, and $c = 5.5\,\text{Å}$ [4]; consequently, YSZ(111) and MgSnN$_2$ would be considered highly mismatched. However, the (100) face of cubic YSZ is better lattice matched to MgSnN$_2$, with a lattice constant of about $a = 5.145\,\text{Å}$ and, thus, was used to grow film WPI-128 based on what was learned in terms of flux and substrate temperature requirements. The exact percentages for the lattice mismatch between the substrates and film are given in Table 3.2.
Table 3.2: Lattice mismatch calculations between the substrates used and predicted MgSnN$_2$ lattice parameters. Notice YSZ(111) has the largest lattice mismatch between the three substrates used.

<table>
<thead>
<tr>
<th>Substrate/Buffer Layer</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ(111)</td>
<td>62.18%</td>
<td>22.57%</td>
<td>51.18%</td>
</tr>
<tr>
<td>YSZ(100)</td>
<td>14.67%</td>
<td>34.11%</td>
<td>6.90%</td>
</tr>
<tr>
<td>ZSN(001)</td>
<td>1.72%</td>
<td>1.47%</td>
<td>1.79%</td>
</tr>
</tbody>
</table>

Film WPI-128 was the first MgSnN$_2$ film to have a crystalline structure, evident from the thin, parallel streaks shown in the RHEED images. The better crystal quality confirmed that by improving the lattice matching between the substrate and the MgSnN$_2$ films, higher quality films can be achieved. Consequently, additional avenues for decreasing the lattice mismatch were explored. Because of previous experience with ZnSnN$_2$ along with it being closely lattice-matched to MgSnN$_2$, the next film was grown with a thin buffer layer of ZnSnN$_2$ on top of YSZ(111) (Fig. 3.3).

Figure 3.3: The RHEED image of the ZnSnN$_2$ buffer layer grown before MgSnN$_2$ film for better lattice matching between the substrate and the film.
For the next film (WPI-129), a ZnSnN$_2$ buffer layer essentially provided a transition layer between the substrate and the MgSnN$_2$ film since the lattice constants for orthorhombic ZnSnN$_2$ are about $a = 5.8$ Å, $b = 6.8$ Å, and $c = 5.6$ Å [6, 55]. ZnSnN$_2$ is able to form a single crystal layer on YSZ(111) since it is slightly better lattice-matched as well as better resembling a hexagonal crystal structure than MgSnN$_2$. The lattice parameters are extremely close between these two materials as seen in Table 3.2, making it much easier to grow a high-quality film. Once the substrates were better lattice-matched to the predicted MgSnN$_2$ lattice parameters, the films formed crystalline materials. The other parameters used to grow these films are provided in Table 3.3.

Table 3.3: Growth parameters for single crystal thin-film MgSnN$_2$.

<table>
<thead>
<tr>
<th>Film #</th>
<th>Substrate/Buffer Layer</th>
<th>Substrate Temperature</th>
<th>Zn Flux atoms/cm$^2$.s</th>
<th>Sn Flux atoms/cm$^2$.s</th>
<th>Mg Flux atoms/cm$^2$.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPI-128</td>
<td>YSZ(100)</td>
<td>610 °C</td>
<td>-</td>
<td>1.30×10$^{13}$</td>
<td>4.12×10$^{14}$</td>
</tr>
<tr>
<td>WPI-129</td>
<td>ZSN/YSZ(111)</td>
<td>425 °C/610 °C</td>
<td>1.50×10$^{15}$</td>
<td>1.30×10$^{13}$</td>
<td>1.33×10$^{15}$</td>
</tr>
</tbody>
</table>
4 Results and Discussion

The improved crystal quality of the fifth and sixth MgSnN$_2$ films are demonstrated by the RHEED images (Fig. 4.1), which supported the information that the lattice matching between the material and the substrate was the leading cause for the films being polycrystalline. To quantify the quality of the films, the full-width half-maximum (FWHM) of the (00) diffraction streak was obtained often fitting to a single Gaussian. Lower FWHM values indicate higher quality films. The calculations for the FWHM of the final two films (Table 4.1) were made at approximately the same thickness and demonstrate that WPI-129 (grown on a ZnSnN$_2$ buffer layer) is a higher quality film than WPI-128 (grown on a YSZ (100) substrate).

![Figure 4.1](image)

**Figure 4.1:** Crystalline RHEED patterns for (a) WPI-128 and (b) WPI-129 taken at the end of growth. These RHEED images demonstrate a streaky pattern instead of the arc patterns characterizing the polycrystalline films, indicating higher quality.
Table 4.1: FWHM of (00) diffraction streak for WPI-128 and WPI-129.

<table>
<thead>
<tr>
<th>Film #</th>
<th>FWHM (Å⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPI-128</td>
<td>0.2367</td>
</tr>
<tr>
<td>WPI-129</td>
<td>0.0882</td>
</tr>
</tbody>
</table>

XRD was used to analyze film WPI-129 by implementing a rod scan to obtain a $\theta$-$2\theta$ plot as seen in Fig. 4.2. Each peak indicates the crystalline plane along the growth direction aligning with the substrate. The sharp, high intensity peak at around 14° is due to the YSZ (111) substrate. If the graph were to continue on to higher angles, there would also be a sharp peak at 28° indicating the (222) plane of the substrate, a peak at 42° indicating the (333) plane, and so on, as those peaks are from parallel planes.

Figure 4.2: $\theta$-$2\theta$ plot for MgSnN$_2$ film WPI-129. Each peak and its corresponding plane is labeled.

The next peak around 16° is much lower in intensity and not as sharp as the YSZ (111) peak, signifying that this is most likely due to the film. This peak is actually a
superposition of two peaks, since features on these type of plots are expected to be symmetrical. The measured $2\theta$ value for each peak was therefore found using a least squares fit with two Gaussian functions. The structural analysis program VESTA [56] was used to determine which planes of MgSnN$_2$ could be attributed to these two peaks. The data for all of the planes is compiled in Table 4.2, which shows that \{002\} and \{210\} planes should show a peak similar to the one seen in Fig. 4.2. Because these two peaks are predicted to be less than a tenth of a degree apart, it is not surprising that these two peaks would together lead to an asymmetrical experimental peak.

Table 4.2: The MgSnN$_2$ planes found by using the structure factors list in VESTA. The predicted $2\theta$ angles as well as their matching interplanar spacing are compared to the corresponding measured values.

<table>
<thead>
<tr>
<th>plane {hkl}</th>
<th>Predicted $d$ (Å)</th>
<th>Predicted $2\theta$ (°)</th>
<th>Measured $d$ (Å)</th>
<th>Measured $2\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>{002}</td>
<td>2.657</td>
<td>15.875</td>
<td>2.6454</td>
<td>15.9424 ± 0.0003</td>
</tr>
<tr>
<td>{210}</td>
<td>2.641</td>
<td>15.968</td>
<td>2.6227</td>
<td>16.0565 ± 0.0003</td>
</tr>
<tr>
<td>{211}</td>
<td>2.365</td>
<td>17.846</td>
<td>2.350</td>
<td>17.963 ± 0.002</td>
</tr>
</tbody>
</table>

The peak around 18° shown in the $\theta$-2$\theta$ plot was originally thought to originate from the ZnSnN$_2$ buffer layer that was grown on YSZ (111) before the MgSnN$_2$ film. However, this layer was so thin (about 10 nm) that it is very unlikely the scan would be able to detect the buffer layer. This indicates that it is probably another MgSnN$_2$ plane, specifically the \{211\} plane. The exact value for this peak was found using a fit with a single Gaussian function. Its presence signifies that the film was likely becoming polycrystalline near the end of growth.

The other plot acquired from XRD analysis on the MgSnN$_2$ film WPI-129, is a pole
plot (Fig. 4.3). This figure should illustrate crystal orientation based on where the highest intensities are measured. At first glance, the intensities seem to demonstrate a wurtzitic crystal structure due to the 60 degree symmetry of the peaks. However, the film was predicted to have an orthorhombic crystal structure with 180 degree symmetry. Since the (002) and (210) planes are so close, both patterns are actually seen in the pole figure. The patterns overlap at the 60° and 240° spots which is why those are so much brighter than the other spots. The wurtzitic pattern is from the unit cell for the surface lattice of the (002) plane and the orthorhombic pattern is from the (210) plane.

![Figure 4.3: Pole plot for the MgSnN$_2$ film WPI-129. The poles at 0, 60, 120, 180, 240, and 300 degrees are from the unit cell for the surface lattice of the (002) plane. There are overlapping poles at 60 and 240 degrees are from the orthorhombic (210) plane. The faint poles at 90, 210, and 330 degrees are from the YSZ (111) substrate.](image)

The lattice parameters (a, b, and c) can be determined using the XRD data. First, the interplanar spacing, $d_{hkl}$, must be calculated. The orthorhombic interplanar spacing can be computed as

\[ d_{hkl} = \frac{\lambda}{Q} \]
\[ \frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \]  

(4.1)

where \(a\), \(b\), and \(c\) are the lattice parameters and \(h\), \(k\), and \(l\) are the Miller indices. From here, the lattice parameters can be calculated using the Bragg equation (Eq. 2.3). \(\theta\) is obtained from the \(\theta\)-2\(\theta\) plot, and the wavelength of the x-ray that was implemented to analyze WPI-129, \(\lambda = 0.7337 \text{ Å}\), allows us to solve for each lattice parameter. The details of the calculation are provided in Appendix A. Both the predicted and measured \(d_{hkl}\) are provided in Table 4.2, while the predicted and measured lattice parameters are given in Table 4.3. The lattice parameter results demonstrate an orthorhombic structure with lattice constants resembling the predictions.

**Table 4.3**: The local density approximation (LDA) and the generalized gradient approximation are used to predict to lattice constants in Jaroenjittichai et al. [4]. The experimentally measured lattice constants are obtained from the XRD results presented in this thesis. The similarities in these results confirm the predicted orthorhombic crystal structure and lattice constants.

<table>
<thead>
<tr>
<th></th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>5.746</td>
<td>6.712</td>
<td>5.313</td>
</tr>
<tr>
<td>GGA</td>
<td>5.932</td>
<td>6.905</td>
<td>5.499</td>
</tr>
<tr>
<td>Measured</td>
<td>5.68293 ± 1×10^{-5}</td>
<td>6.81690 ± 1×10^{-5}</td>
<td>5.29078 ± 1×10^{-5}</td>
</tr>
</tbody>
</table>

The value

\[ Q = \frac{2\pi}{d_{hkl}} \]  

(4.2)

on the pole plot is the magnitude of the reciprocal lattice space vector. Estimated interplanar values can be found in VESTA and these values and the measured values are shown in Table 4.2. Since the magnitudes of the reciprocal lattice space vectors would be very close for both the (002) and (210) planes (both about 2.385 Å\(^{-1}\)), it
makes sense that these planes would appear in the same pole plots.

A series of RHEED images are taken during the first few minutes of every growth experiment to determine another important parameter, the growth rate (Table 4.4). The calculations are made by measuring the periodicity of the intensity oscillations of specularly reflected (non-diffracted) electrons. These oscillations are made by the changing roughness of the surface as each monolayer is achieved. If the surface is rough, more electrons are scattered and intensity is reduced. Once the monolayer is complete, the surface will be smooth, meaning less electrons will be scattered. Therefore, every time a RHEED image is at its highest intensity, one monolayer has been grown [57]. Since the growth rate can be determined within the first few minutes of growth, the amount of time needed to grow the film to a desired thickness can be calculated. To achieve a reasonable thickness for these films, the growth rate will need to be improved by possibly increasing the fluxes of the elements or decreasing the growth temperature. However, since an increase in growth temperature correlated with an improvement in crystal quality, other parameters may need to be altered to maintain a high quality crystal structure.

**Table 4.4:** Growth rates, the amount of time taken to grow each film, and the final thickness of each film.

<table>
<thead>
<tr>
<th>Film #</th>
<th>Growth Rate (nm/hr)</th>
<th>Time Span (minutes)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPI-124</td>
<td>121.0</td>
<td>100</td>
<td>201.7</td>
</tr>
<tr>
<td>WPI-125</td>
<td>147.6</td>
<td>73</td>
<td>179.6</td>
</tr>
<tr>
<td>WPI-126</td>
<td>93.2</td>
<td>90</td>
<td>139.8</td>
</tr>
<tr>
<td>WPI-127</td>
<td>67.4</td>
<td>80</td>
<td>89.9</td>
</tr>
<tr>
<td>WPI-128</td>
<td>53.3</td>
<td>123</td>
<td>109.3</td>
</tr>
<tr>
<td>WPI-129</td>
<td>79.9</td>
<td>105</td>
<td>139.8</td>
</tr>
</tbody>
</table>
Absorption edge measurements were taken by collaborator Prof. Roger Reeves at the University of Canterbury using optical transmission spectroscopy to therefore be able to extrapolate the optical band gaps of each material. These measurements were made by measuring the transmission of light by the sample as a function of wavelength. The sharp rise (absorption edge) of the absorption spectrum emerges at wavelengths where the energy of an absorbed photon from the incident beam correlates with the optical band gap energy of the sample [58]. Tauc plots are a way to visualize these data and determine the optical band gap, as shown in Fig. 4.4 [59].

![Absorption edge measurements](image)

**Figure 4.4:** Tauc plots to determine the optical band gap of each film. The extrapolated line is a least squares linear fit to the linear segment of the absorption edge data. The x-intercept indicates the optical band gap [60].

The Tauc plots indicate that the MgSnN$_2$ films have a rather wide range of band gaps, varying from 2.57 eV to 3.325 eV. MgSnN$_2$ is a heterovalent ternary nitride that belongs to the orthorhombic space group Pna2$_1$. However, it has been shown that in some heterovalent ternary materials, an increase in disorder in the cation sublattice can lead to an increase in symmetry, resulting in the II-IV-V$_2$ having a wurtzitic structure like its analogous III-V materials [5, 33]. Studies of disorder in compounds date back to
experimental observations of Cu$_3$Au alloys [61–63] and similar phenomena were later observed in III-V isoelectronic alloys such as Ga$_x$In$_{1-x}$P$_2$ [64,65]. In cases such as these, the method for quantifying the degree of ordering is the long-range order parameter $S$. The order parameter equation can be described as

$$S = r_\alpha + r_\beta - 1$$

where, in the case of MgSnN$_2$, $r$ is the fraction of Mg sites occupied by Mg atoms and $r$ is the fraction of Sn sites occupied by Sn atoms [66]. The films in this study are stoichiometric, meaning that the amount of Mg on Sn sites will be equal to the amount of Sn on Mg sites making $r_\alpha = r_\beta = r$ [6]. Typically, to be able to determine the order parameter experimentally, x-ray diffraction measurements are taken with ratios of the integrated intensity of superlattice reflections to fundamental reflections [5, 6, 60]. Additionally, long-range order parameters can be determined through RHEED by plotting the intensity profile of the (00) feature, and taking the ratio of integrated intensities [60]. In the case of MgSnN$_2$, a binary system, the intensity of a superlattice peak will decrease as the disorder of the system increases making the order parameter $S$ directly proportional to the structure factors of the superlattice peaks [5, 6].

The two ordering extremes can be visualized as in Fig. 4.5. Parameters including the substrate temperature, the metal fluxes, and the nitrogen flux that are controlled during film growth are the main contributors to the variation of cation sublattice ordering. Since the optical band gap and order parameter has been calculated for each film [60], the clear correlation demonstrated in Fig. 4.6 verifies that the order parameter can vary the band gap of MgSnN$_2$. The capability to adjust the band gap can also prove to be an advantage over III nitrides, as it removes the need for alloys [5, 6, 60].
Figure 4.5: Possible lattice structures of MgSnN$_2$, shown looking along the c-axis. Mg is represented by orange atoms, Sn is represented by blue atoms, and N is represented by yellow atoms. The unit cells are outlined. a) The ordered cation sublattice with an orthorhombic crystal structure. b) The disordered cation sublattice with a wurtzitic crystal structure. Notice the atoms that are colored both orange and blue represents that either Mg or Sn could occupy those sites.

Figure 4.6: Optical band gap for the series of MgSnN$_2$ films exhibiting a linear relationship with respect to the square of the order parameter $S$. The order parameter was measured by RHEED and confirmed by Raman spectroscopy [60].
Raman spectroscopy analysis completed by Prof. Patrice Miska of Université de Lorraine was also used to evaluate the MgSnN$_2$ films. Raman spectroscopy involves using an incident, monochromatic light (in this case, a green laser) to observe the vibrational modes in the sample. Raman scattered light is frequency-shifted as a result of inelastic scattering with respect to the incident frequency to either a lower or higher frequency [67, 68]. Thus, when a laser interacts with molecular vibrations, the energy of the laser will be shifted either up or down depending on the vibrational modes of the sample. The resulting spectra are plotted as shown in Fig. 4.7 [60].

![Raman Spectra of MgSnN$_2$ Films](image)

**Figure 4.7:** Raman spectra of MgSnN$_2$ films. The top profile is most alike to a wurtzite structure, meaning it has the highest degree of cation disorder and the lowest $S^2$ value. The bottom profile is most alike to an orthorhombic structure meaning it has the lowest degree of cation disorder and highest $S^2$ value. Varying degrees of cation ordering are found in the spectra in between [60].

Different features are prominent depending on the crystal structure of that sample, as the lattice periodicity (symmetry) is varied. From Fig. 4.7 it is evident that the crystal
structure varies between each MgSnN$_2$ film. These results are comparable to the ones found when analyzing the varying degrees of disorder from RHEED analysis. Much like RHEED, the order parameter $S^2$ can be calculated using the Raman spectra results. The order parameter using Raman results can be calculated by taking the ratio of the integrated intensities of one of the ordered peaks and one of the disordered peaks. The calculation for the order parameter $S^2$ for each of the films using the Raman data are the same (to two significant digits) as the order parameters calculated using RHEED as seen in Fig. 4.6.
5 Conclusions

5.1 Accomplishments

This project focused on discovering the parameters needed to synthesize high quality, thin-film materials of MgSnN$_2$. At the onset of the project, this material had yet to be synthesized and only theoretical predictions of the properties had been made. Because of the predicted near-ultraviolet band gap of MgSnN$_2$, the material offers a conceivably eco-friendly, cost effective alternative for LEDs and other opto-electronic devices.

Since MgSnN$_2$ had not been synthesized before this work, the growth of the first film was based upon previous knowledge gained from growing ZnSnN$_2$ as well as the calculated temperatures needed to grow at the desired Mg:Sn flux ratio. Parameters such as Mg:Sn ratio and substrate temperature were updated iteratively to further improve the film quality. However, the lattice mismatch between the original (111) YSZ substrate used and MgSnN$_2$ needed to be addressed before high quality growth of this material could be achieved. One film was grown on YSZ (100) and another was grown on a buffer layer of ZnSnN$_2$. As a result of these changes, the quality of the films notably improved.

Additionally, this work has also characterized the MgSnN$_2$ films grown via PAMBE. The lattice parameters were extrapolated from XRD measurements and compared to the theoretical calculations showing very good agreement. The optical band gap measurements were calculated from absorption edge data. The crystal orientation was illustrated by the pole figure from the XRD data. Additionally, the thickness of each of
the films was calculated by measuring the periodicity of the oscillations of the RHEED streaks.

5.2 Observations

The absorption edge measurements analyzed in the Tauc plots indicate that MgSnN$_2$ is able to cover a wide range of band gaps, approximately 2.57 eV to 3.325 eV. Through analysis of the RHEED and Raman spectra, differing degrees of cation disorder were found to exist. Comparing the degree of cation disorder to the optical band gaps demonstrated a linear relationship that has also been found in other heterovalent ternary nitride materials such as ZnSnN$_2$ [5, 6, 33, 60]. There are ways to control the order parameter of a material through different substrate temperatures and elemental fluxes; thus, the order parameter provides a way to tune the band gaps without alloying. Together both ZnSnN$_2$ and MgSnN$_2$ are able to span a range of band gaps from 1 eV to 3.4 eV, which covers the range of band gaps materials comprised of gallium and indium can reach [60]. Therefore, these ternary heterovalent semiconductors could be an eco-friendly alternative to the current semiconductor materials.

The experimentally measured lattice constants strongly correlate to the orthorhombic measurements found by Jaroenjittichai and Lambrecht [4]. However, the XRD results alongside the optical band gap measurements indicate that the lattice parameters can change, thus resulting in a wurtzitic structure. The change in crystal structure comes from differing degrees of cation disorder. By altering the growth parameters of MgSnN$_2$, we are able to control the degree of cation disorder allowing us to tune between a wide range of band gaps without alloying.
5.3 Further Work

There is still much left to discover and problems to solve in the research of MgSnN\(_2\). For this new semiconductor to be feasible for future devices, the growth rate must be improved. Currently, the high substrate temperature makes it difficult for atoms to remain on the surface without desorbing. Lowering the substrate temperature would mean altering other parameters to be able to still achieve high quality films. Based on ZnSnN\(_2\), it is possible that increasing the Sn flux and most likely the N\(_2\) flux will lead to improved growth rates. Higher growth rates will lead to thicker films, which are needed to be able to conduct additional measurements to determine the minority carrier lifetimes and impurity levels of the material.

Other measurements will need to be made on current films as well as other prospective films to further expand the knowledge of MgSnN\(_2\) and whether device quality can be attainable. RBS measurements were not able to be obtained to determine the exact composition of our materials due to the low atomic mass of both magnesium and nitrogen. These elements do not appear in the backscattering spectra because of the larger elements (oxygen and yttrium) in the YSZ substrate. One solution would be to place a glassy carbon substrate alongside the YSZ substrate while growing the next MgSnN\(_2\) film. Because carbon has an atomic mass below Mg and N, the respective peaks on the spectra would be evident. Hall effect measurements should also be performed to determine the conductivity and carrier concentration of the films. The goal is to achieve intrinsic conductivity and then investigate possible dopants to be able to create a pn junction. The formation of a pn junction is necessary before the material can be incorporated in most device applications.

Another possible avenue for this material would be exploring the ability to make quantum well devices. Quantum wells are nanostructures formed in semiconductors
by having a narrow band gap material sandwiched between two wider band gap
materials [69]. The ability to tune the band gap of MgSnN₂ opens up the possibility
for it to be part of a quantum well structure with either ZnSnN₂ or even itself.
Additionally, this material is closely lattice matched to ZnSnN₂, making it easier
for the two materials to be layered on top of each other as already proven in this
study. Quantum wells can increase optical gain (important for semiconductor lasers),
increase the radiative recombination rate, and have efficient carrier capture times.
Quantum wells have been proven to be useful for creating lasers [70], solar cells [71],
and LEDs [72].

Consequently, MgSnN₂ has the potential to be a future eco-friendly, low cost
alternative for current wide band gap devices comprised of expensive and low-earth-
abundant elements, such as indium and gallium.
Appendices

Appendix A: Calculating Lattice Constants for WPI-129

\[
\frac{1}{d_{002}^2} = \frac{0^2}{a^2} + \frac{0^2}{b^2} + \frac{2^2}{c^2} \quad (5.1)
\]

\[d_{002} = \frac{c}{2} \quad (5.2)\]

\[\lambda = 2d_{002}\sin(\theta_{002}) \quad (5.3)\]

\[0.7337 = 2\left(\frac{c}{2}\right)\sin(7.9712) \quad (5.4)\]

\[c = 5.291 \text{ Å} \quad (5.5)\]

\[
\frac{1}{d_{210}^2} = \frac{2^2}{a^2} + \frac{1^2}{b^2} + \frac{0^2}{c^2} \quad (5.6)
\]

\[d_{210} = \sqrt{\frac{1}{\frac{4}{a^2} + \frac{1}{b^2}}} \quad (5.7)\]

\[\lambda = 2d_{210}\sin(\theta_{210}) \quad (5.8)\]

\[0.7337 = 2\left(\frac{1}{\frac{4}{a^2} + \frac{1}{b^2}}\right)\sin(8.0283) \quad (5.9)\]
\[ \frac{1}{d_{211}^2} = \frac{2^2}{a^2} + \frac{1^2}{b^2} + \frac{1^2}{5.291^2} \]  \hspace{1cm} (5.10)

\[ d_{211} = \sqrt{\frac{1}{\frac{4}{a^2} + \frac{1}{b^2} + 0.03572}} \]  \hspace{1cm} (5.11)

\[ \lambda = 2d_{211}\sin(\theta_{211}) \]  \hspace{1cm} (5.12)

\[ 0.7337 = 2\sqrt{\frac{1}{\frac{4}{a^2} + \frac{1}{b^2} + 0.03572}}\sin(8.9815) \]  \hspace{1cm} (5.13)

Solve equations 5.9 and 5.13 for \( a \) and \( b \) since there are two equations, two unknowns.

In order to calculate the \( a \) and \( b \) lattice parameters, 2D Newton’s method for root finding was implemented. Values for \( a \), \( b \), and \( c \) can be found in Table 4.3.
Appendix B: List of Films and Their Growth Parameters

Table B1: The parameters of every MgSnN$_2$ film in this thesis. Additionally, every film had a N$_2$ flow of 12.5%, a N$_2$ pressure of $2.66 \times 10^{-5}$, and a plasma power of 150 W.

<table>
<thead>
<tr>
<th>Film #</th>
<th>Substrate/ Buffer Layer</th>
<th>Substrate Temperature</th>
<th>Sn Temperature</th>
<th>Sn Flux $10^{13}$ atoms/cm$^2$·s</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPI-124</td>
<td>YSZ(111)</td>
<td>425 °C</td>
<td>1020 °C</td>
<td>1.05</td>
</tr>
<tr>
<td>WPI-125</td>
<td>YSZ(111)</td>
<td>425 °C</td>
<td>1030 °C</td>
<td>1.06</td>
</tr>
<tr>
<td>WPI-126</td>
<td>YSZ(111)</td>
<td>580 °C</td>
<td>1030 °C</td>
<td>1.12</td>
</tr>
<tr>
<td>WPI-127</td>
<td>YSZ(111)</td>
<td>610 °C</td>
<td>1030 °C</td>
<td>1.20</td>
</tr>
<tr>
<td>WPI-128</td>
<td>YSZ(100)</td>
<td>610 °C</td>
<td>1030 °C</td>
<td>1.30</td>
</tr>
<tr>
<td>WPI-129</td>
<td>ZSN/YSZ(111)</td>
<td>425 °C/610 °C</td>
<td>1030 °C</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Table B2: Note that the Zn cell was shuttered after growth of the buffer layer.

<table>
<thead>
<tr>
<th>Film #</th>
<th>Mg Temperature</th>
<th>Mg Flux $10^{14}$ atoms/cm$^2$·s</th>
<th>Zn Temperature</th>
<th>Zn Flux $10^{15}$ atoms/cm$^2$·s</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPI-124</td>
<td>410 °C</td>
<td>7.88</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WPI-125</td>
<td>445 °C</td>
<td>9.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WPI-126</td>
<td>445 °C</td>
<td>7.22</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WPI-127</td>
<td>460 °C</td>
<td>8.39</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WPI-128</td>
<td>480 °C</td>
<td>4.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WPI-129</td>
<td>480 °C</td>
<td>13.3</td>
<td>325 °C</td>
<td>1.50</td>
</tr>
</tbody>
</table>
References


