GROWTH AND CHARACTERIZATION OF BISMUTH TRI-IODIDE SINGLE CRYSTALS BY MODIFIED VERTICAL BRIDGMAN METHOD

By

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With my deepest love to my entire family
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Bismuth tri-iodide (BiI$_3$) is a wide band gap semiconductor material with potential for room temperature gamma-ray detection applications. The inability to produce high quality, pure, and large single crystals is one of the major challenges for this material preventing its use in gamma-ray detection. This work presents the growth and characterization of BiI$_3$ single crystals by a modified vertical Bridgman (MVB) method.

The growth parameters to produce BiI$_3$ single crystals were explored by adjusting growth rate and temperature gradient at the solid-liquid interface. Single crystals of BiI$_3$ have been successfully grown in Pyrex glass ampoule at different growth conditions. Through etch pit density (EPD) and X-ray rocking curve measurement, the crystal with the best quality was determined to be obtained at 0.5 mm/h growth rate and 10°C/cm temperature gradient. Single crystal (001) oriented slabs up to 18 x 13 x 5 mm$^3$ (the largest BiI$_3$ single crystal ever reported) were obtained under this condition. Impurity characterization on the starting BiI$_3$ powder and the grown crystals indicated a relatively high total impurity concentration up to $10^{17}$ cm$^{-3}$, and the crystal growth using Pyrex glass does not introduce additional impurities to the crystal.
The energy band gap is an important parameter for materials used as a room temperature gamma-ray detector, as it determines the energy to produce an electron-hole pair which is the source of the signal for the detector. Remarkably, very different band gap characteristics and values of BiI₃ have been reported in literature. This study characterized the band gap of BiI₃ through Ultraviolet-visible spectroscopy (UV-Vis), which yielded an indirect band gap of 1.68 ± 0.09 eV at room temperature. Impurity and temperature effects, as commonly observed in many semiconductors, have been investigated as the major extrinsic factors that influence the band gap value of BiI₃.

Three different metals, Au, Pd, and Pt were sputtered on the surface of BiI₃ single crystal for fabrication of the electrode. The metal-BiI₃ interface was characterized by X-ray photoelectron spectroscopy (XPS). Chemical reactions were observed for the surface sputtered with Pd and Pt electrode, while no reaction was observed on the surface with Au electrode. It was proposed that Au should be used for the contact material for BiI₃. Current-voltage characterization indicated that BiI₃ crystal with Au electrode exhibited the highest resistivity with values in the order of magnitude of $10^9$ Ω·cm, which is sufficiently large for the application of a room temperature gamma-ray detector. Based on the work presented in this dissertation, a series of avenues for future work are presented to be able to take this material into actual devices.
CHAPTER 1
INTRODUCTION

1.1 Statement of Problem and Motivation

Gamma-ray detectors have become increasingly important for the applications of medical imaging, environmental safety, and homeland security. Most of these applications desire a portable device with high gamma-ray energy resolution and detection efficiency, compact size, room-temperature operation, and low cost. The most widely used gamma-ray detectors include gas-filled detectors, scintillation counters, and semiconductor detectors, among which semiconductor detectors received most of the attention due to their much better energy resolutions.

The great success of high purity Ge and Si detectors encouraged the discovery and development of new semiconductor materials for radiation detection.\(^1\) The operation of high purity Ge and Si detectors requires liquid N\(_2\) cooling due to their small band gaps, resulting in a bulky and heavy system that limits their use. Compound semiconductor materials with large band gap overcome this limit and become the most promising candidates as an alternative to high purity Ge and Si. In the past few decades, many compound semiconductor materials have been extensively studied. Although not all of these materials are readily available for gamma-ray detection, several compound semiconductors including CdTe, CdZnTe, and Hgl\(_2\) have demonstrated significant energy resolution and detection efficiency.\(^2\) Even though CdTe and CdZnTe have been commercialized for almost 25 years, the high cost of fabrication and limited supply of high quality crystals prevent the large scale production.\(^3\) The discovery and development of new materials is still the main focus of current research for room temperature gamma-ray detectors.
BiI₃ is a wide band gap semiconductor material that has a potential for room temperature gamma-ray detection and spectroscopy. This material has a much higher effective atomic number than Ge and Si, thus has higher gamma-ray detection efficiency. Unfortunately, the growth of large volume and high quality crystals remains as the major challenge for BiI₃ to be commercialized. The present work focuses on the growth and evaluation of BiI₃ single crystals which are grown by a modified vertical Bridgman method. The general material properties of BiI₃ (hardness, band gap, electrical resistivity, etc.) have also been investigated.

1.2 Scientific Approach

BiI₃ has a low melting point of 408°C. Unlike HgI₂ which experiences a phase transformation from α-HgI₂ to β-HgI₂ below melting point, BiI₃ is stable within the range from the melting point to room temperature, as shown in the Bi-I phase diagram (Figure 1-1).⁴ BiI₃ was reported to have a vapor pressure of around 90 mbar at the melting point and 1 – 13 mbar at temperatures of 250°C to 300°C.⁵-⁶ Therefore BiI₃ single crystals can be grown from both liquid and vapor phases. Single crystals of BiI₃ have been successfully grown by physical vapor transportation (PVT) method⁷-¹⁰ and vertical Bridgman technique.¹¹-¹²

For the application of gamma-ray detection, single crystal with large volume (~1 cm³) is desired as higher interaction volume increases the detection efficiency. While PVT method generally produces crystals with small volumes up to several mm³, vertical Bridgman technique has the potential to grow much larger crystals up to tens of cm³. Therefore, the present work chooses vertical Bridgman technique to grow BiI₃ single crystals with some modifications.
As crystal growth is a time-consuming process, the temperature profile has been carefully designed and tested. Due to the unavailability of the thermal properties of BiI₃, the growth conditions have been determined on an educated initial guess basis. The grown single crystals were characterized by various techniques and research tools. The crystal structure was identified by X-ray diffraction (XRD). The crystal quality was characterized by etch pit density (EPD) measurement and X-ray rocking curve ω-scans. The impurity concentration in the crystal was characterized by inductively coupled plasma - atomic emission spectroscopy (ICP-AES). The surface morphology was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The elemental composition of the crystal was characterized by X-ray photoelectron spectroscopy (XPS).

The band gap of BiI₃ has been reported with different values and characteristics. This work investigated the band gap of BiI₃ through UV-Vis transmission and reflection spectra. By comparing and analyzing the results obtained from ellipsometry and theoretical calculation using density functional theory (DFT), the band gap of BiI₃ was
determined, and the factors that affect the band gap were analyzed to provide possible solution to the discrepancy.

Palladium and gold have been used as the electrical contact materials for BiI$_3$.$^{12-13}$ This work investigated the interface between BiI$_3$ single crystal and different contact materials of Au, Pd, and Pt using XPS. The morphology of the electroded surface was characterized by AFM. The resistivity of BiI$_3$ with different electrode was determined by measuring the I-V characteristic. The compatibility of these contact materials with BiI$_3$ was determined by the above characterizations.

Finally, based on the study of this work, suggestions for future work are proposed for better control of crystal growth and post-growth treatment.

1.3 Organization of Dissertation

Chapter 2 provides a background that covers the fundamentals of gamma-ray detectors and some material properties of BiI$_3$. The compound semiconductors that have been studied for room temperature gamma-ray detector are discussed in detail. The purpose of this is to help the reader understand the working principles and the important material properties of a gamma-ray detector. The crystal structure of BiI$_3$ and structure related optical properties are discussed following the detector description. Then the fundamental thermodynamics of crystal growth including nucleation and the crystal growth interface are discussed. Finally, the previous research of developing BiI$_3$ towards a room temperature gamma-ray detector is summarized to provide the reader the background of this work.

Chapter 3 discusses the crystal growth by a modified vertical Bridgman (MVB) and PVT method. An in depth discussion on the thermodynamics of vertical Bridgman and PVT growth is presented. The detailed growth procedures and crystal characterizations
are described and results are presented. The relationship between the growth conditions and the crystal quality is discussed.

Chapter 4 discusses the band gap characterization of BiI$_3$ single crystals. The previous work with different band gap values and characteristics is reviewed. The experimental results on UV-Vis spectra and impurity characterization are presented. The possible reasons causing the discrepancy in literature about the band gap are discussed.

Chapter 5 discusses the BiI$_3$-electrode interface characterized by XPS. The elemental compositions on BiI$_3$ surface with Au, Pd, and Pt electrode are presented and discussed. The resistivity of BiI$_3$ with different electrodes is compared. Recommendation for the electrode material of BiI$_3$ is given based on the experimental results.

Finally in Chapter 6, a summary of the dissertation is presented and the future work in the relevant research areas is discussed.

At the end of the dissertation, four appendices are provided. Appendix A presents the purification results of BiI$_3$ powder using sublimation and vertical zone melting method; Appendix B presents the attempts to grow BiI$_3$ single crystal with different diameters using MVB method; Appendix C presents the sample preparation of BiI$_3$ single crystal for TEM characterization using focused ion beam (FIB) technique; Appendix D presents the synthesis of sodium potassium niobate ($\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_5$, NKN) for the application of piezoelectric transformer.

1.4 Contributions to the Field

The main contributions of this dissertation to the development of BiI$_3$ single crystal as a room temperature gamma-ray detector are summarized as follows:
• The complete temperature profile of growing BiI₃ single crystals using MVB method was established. The parameters including heating rate, soaking temperature and time, ending temperature of crystal growth, and post-growth cooling rate were determined.

• The growth conditions of producing large volume BiI₃ single crystals were determined for MVB method, resulting in the largest grown BiI₃ single crystal ever reported (18 x 13 x 5 mm³).

• The procedures to measure the etch pit density of BiI₃ single crystals were established. The etchant concentration and etching time were determined and could serve as a standard for BiI₃ single crystal.

• The possible solutions to the discrepancy of band gap values and characteristics for BiI₃ were proposed.

• The proper electrode material for BiI₃ single crystal was determined to be Au. The result suggested that using Pd as the electrode for iodide compound may not be appropriate. This will lead to the re-evaluation of the electrode materials for all the iodine based compound semiconductors such as Hgl₂ and Pbl₂.


CHAPTER 2
BACKGROUND

2.1 Types of Gamma-ray Detectors

Gamma-rays interact with materials primarily through three mechanisms: photoelectric absorption, Compton scattering, and pair production. In the photoelectric absorption process, the photon transfers all its energy to an orbital electron. This photoelectron then interacts with the lattice of the detector material and creates many electron-hole pairs until it completely loses its kinetic energy. In the Compton scattering process, the photon only transfers partial of its total energy to an orbital electron leaving the material with a degraded photon. In the pair production process, a photon with energy higher than $2m_ec^2$ interacts in the vicinity of a nucleus and produces an electron and a positron pair. Based on which interaction mechanism the gamma-ray detector utilizes, there are two broad classes of gamma-ray detectors. The first is generally called gamma-ray spectrometer which records the gamma-ray energy by collecting photoelectrons. These types of detectors include gas-filled detectors, scintillation counters, and semiconductor detectors. The second class of detectors includes those used in gamma-ray telescopes and imaging systems. Detectors of this type register the direction and energy of the incoming gamma-rays through Compton scattering or pair production. Here the discussion will be focused on gamma-ray spectrometers.

2.1.1 Gas-Filled Detectors

Gas-filled detectors consist of a metal vessel filled with gas (argon or helium), a gamma-ray transparent window (such as Be or mylar), and a center wire functioning as an anode. A high voltage is maintained between the metal vessel and the anode (Figure 2-1). When high energy rays or particles collide with an inert gas atom, they...
ionize the atom and transfer a massive amount of energy to an outer shell electron, known as photoelectron. The photoelectron releases its excess kinetic energy by subsequently colliding with other outer shell electrons. As a result, a cascade of accelerated electrons are collected by the anode and detected as an electrical pulse.

Figure 2-1. General schematic of a gas-filled detector. Diagram after Ahmed.\textsuperscript{16}

If the voltage between the electrodes is increased, the electrons will obtain enough kinetic energy to cause further ionizations. By controlling the gas pressure and the operation voltage, a proportional counter can be tailored and constructed such that the output signal is proportional to the deposited gamma-ray energy. Proportional counters have been used for gamma-ray spectroscopy with low energy detection (< 100 keV).\textsuperscript{17}

If the operation voltage is further increased, charge multiplication increases (avalanches) until the space charge produced by the residual ions inhibits further ionization. As a result, the collected charge pulse is no longer proportional to the energy deposited in the gas. This type of detector is known as the Geiger-Mueller (GM) detector.\textsuperscript{15} A GM tube detector does not differentiate the energies of the particles it
detects; it only counts the number of particles entering the detector. This type of
detector is widely used for β-γ dosimetry in health physics.17

Gas-filled detectors account for only a small portion of gamma-ray spectrometers.
The scintillation and semiconductor detectors are much more desirable for obtaining the
spectroscopic detail of gamma-rays in the energy range from 100 to 1000 keV.

2.1.2 Scintillation Counters

A scintillation counter consists of two main components: a scintillator and a
photomultiplier tube (PMT). A scintillator is a material that emits low energy photons
(usually in the visible range) when absorbing radiation. The light produced from the
scintillation process is then converted to electrical signal by a PMT. A PMT is normally
composed of a photocathode, an electron-multiplier section, and an anode.17 The
photocathode has the unique characteristic of producing electrons when light strikes on
its surface. These electrons are accelerated through a series of secondary emission
electrodes (known as dynodes), knocking out a number of new electrons subsequently,
multiplying their number in each step. After multiplication, the electrons are collected by
an anode to form an electronic pulse (Figure 2-2). In a typical PMT, the multiplication
factor is on the order of $10^7$.14

![Diagram of a scintillation counter](image)

Figure 2-2. Scheme of a scintillation counter. The scintillator and PMT are often
optically linked by a light pipe. Diagram after Hastings and Marcia.17
Scintillators can be made of organic or inorganic materials, depending on the intended applications. Inorganic scintillators are more widely used due to their stability and higher density which leads to higher detection efficiency. Examples of organic scintillators are organic crystals, plastics, and liquids. Organic crystal scintillators are composed of aromatic hydrocarbons such as anthracene ($\text{C}_{14}\text{H}_{10}$). They are very durable but hard to be machined. However, they are not often used due to the lack of success to grow large single crystals. Plastic scintillators are solutions of fluorescent organic compounds dissolved in a solidified polymer matrix. Plastic scintillators give fast signal and relatively high light output. They can also be easily shaped and machined to the forms desired in detectors. Due to their low intrinsic scintillation efficiency, plastic scintillators are not suitable for detection of lower energy gamma-rays and cannot be used for gamma-ray spectroscopy. However, they are useful for gross counting gamma-rays with energies higher than 100 keV. Their relatively low cost and availability as large size sheets make them the most widely used scintillators. Liquid scintillators are fluid solutions with similar fluorescent organic compounds as in plastic scintillators. They can be easily loaded with other additives such as wavelength shifters to match the spectral sensitivity range of a particular PMT. Liquid scintillators are normally required to be sealed to avoid the degradation caused by dissolved oxygen.

Inorganic scintillators are usually made of alkali halides (i.e., NaI, CsI) in which the high $Z$ component enhances the photoelectric interaction efficiency. Bismuth germanate ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$, BGO) is another popular scintillation material which has a very high gamma-ray counting efficiency, but low energy resolution. When gamma-rays interact with scintillation materials, electrons can jump up to higher energy levels...
through excitation, then relax back to a lower energy state by emitting photons of light. In a pure inorganic scintillation material, the relaxation with the emission of a photon has very low efficiency. Furthermore, the emitted photons usually possess higher energy to which the PMT is sensitive. Small amount of impurities (activators) are often added to the scintillator to enhance the emission of visible photons. Thallium and sodium are often used for this purpose. For scintillation detector described as NaI(Tl), it means that it is a sodium iodide crystal with a thallium activator. Inorganic scintillators have been widely used in process industry, nuclear medicine, life sciences, and many space-based missions to observe sources of cosmic gamma-radiation.17

2.1.3 Semiconductor Detectors

In semiconductor detectors, the charge produced by the photon interactions is directly collected. Gamma-rays incident to the detector excite electron-hole pairs in proportion to the energy deposited in the detector (Figure 2-3). By applying a voltage across contacts on opposite sides, these free charges will drift through the detector and create an induced charge on the electrodes proportional to the distance traveled by the electrons and holes, as described by Shockley-Ramo theorem,20-21

\[ dQ = \frac{qN_0}{L} dx \]  

(2-1)

where Q is the induced charge, N₀ is the initial number of electron-hole pairs, and L is the detector thickness. These charges are integrated by an external circuit and a pulse height spectrum is generated with the peak positions in the spectrum proportional to the energies of the incident photons. If the charge trapping can be ignored, the total induced charge is equal to the initial created charge, Q = qN₀. However, for most compound semiconductors some extent of charge traps are always present and the loss
from charge carrier trapping has to be taken into account. The charge collection
efficiency (CCE) describes the fraction of charges that reach the electrodes, and is
given by the Hecht equation:22

\[
CCE = \frac{Q}{Q_0} = \frac{v_e T_e}{L} \left[ 1 - \exp\left(-\frac{(L-x)}{v_e T_e}\right) \right] + \frac{v_h T_h}{L} \left[ 1 - \exp\left(-\frac{x}{v_h T_h}\right) \right]
\] (2-2)

where L is the detector thickness, x is the distance from the cathode to the location of
the radiation interaction, ve and vh are the drift velocity of electrons and holes, and \( \tau_e \)
and \( \tau_h \) are the electron and hole lifetimes. Equation (2-2) indicates that the CCE
depends not only on the mean free paths \((\nu \tau)\) of electrons and holes, but also on the
location where the charges are created. This provides ways to improve the detector
energy resolution for a specific material by varying the detector shape, contact
groupmetry, and detector configurations.14,20,23-24

Figure 2-3. Basic operating configuration of a planar detector.

The energy resolution of semiconductor detectors is dramatically higher than that
of a scintillation or gas-filled detector, which makes it an excellent candidate for gamma-
ray spectroscopy. Lithium-drifted germanium (Ge(Li)) detectors were developed in the
early 1960s25 and remained the most popular design for gamma-ray spectroscopy for
two decades. Lithium is drifted through the material to compensate the residual
acceptor impurities after the crystal has been grown. The drifted region can easily be depleted over its entire thickness which allows charges (electrons and holes) to move freely during the charge collection process. In the early 1980s, high-purity Ge (HPGe) became widely available and rapidly replaced Ge(Li). Whereas Ge(Li) detectors must be continuously maintained at liquid nitrogen temperature (77 K) to keep the lithium drifting at a frozen stage, HPGe detectors can be allowed to warm to room temperature between uses. This provides a much greater operational convenience and simplifies the fabrication of detectors. In general, Ge(Li) and HPGe detectors have essentially identical detection efficiency and energy resolution. Besides Ge, lithium drifted Si (Si(Li)) has also been successfully fabricated for gamma-ray spectrometer. A disadvantage for single element semiconductor detectors is that they must be operated at low temperatures to reduce the thermally generated leakage current, resulting in a bulky system that limits their use in the field. In principle, compound semiconductors with a wider bandgap (greater than 1.5 eV) could reduce this thermally generated leakage current so that operation at room temperature is possible. However, since Van Heerden first demonstrated that silver chloride (AgCl) crystal was able to detect gamma-ray and alpha particles in 1945, compound semiconductors have experienced slow development over the years, largely due to the difficulties of obtaining large volumes, impurities and defects free crystals. So far the most widely explored compound semiconductors for room temperature gamma-ray detection are CdTe, Cd$_{1-x}$Zn$_x$Te, and HgI$_2$, which will be discussed in detail in the following section.

Photoelectric absorption is the favored gamma-ray interaction for a spectrometer since only this process leads to the total absorption of the incident energy. The
interaction cross-section for photoelectric absorption varies as $N Z^5$, where $N$ is the number of atoms per unit volume and $Z$ is the effective atomic number. Thus, high $Z$ material should be chosen for efficient gamma-ray spectroscopy. This makes another advantage of compound semiconductor detectors over single element detectors by incorporating high $Z$ elements in the compounds. For semiconductor compounds, the photoelectric absorption is most influenced by the element with the highest atomic number, instead of the average $Z$. For example, based on the XCOM Photon Cross Sections Database from NIST, while both GaAs and InP have the same average $Z$, InP has two to three times higher absorption coefficients in the hard X-ray region due to the higher $Z$ of In (49) compared to Ga (31) and As (33). Therefore, the much higher atomic numbers of semiconductor materials, such as CdTe ($Z_{Te} = 52$) and HgI$_2$ ($Z_{Hg} = 80$), determine the significantly higher photoelectric absorption than Ge ($Z = 32$) and Si ($Z = 14$). The detection efficiency per unit volume will therefore be higher.

### 2.2 Materials for Room Temperature Semiconductor Detector

The general material requirements for a room temperature gamma-ray detector include high density and atomic numbers, which lead to superior energy resolution and detection efficiency; moderate bandgap between 1.5 eV and 3 eV, which prevents thermally generated leakage current at room temperature and allows as many electron-hole pairs to be excited, and high resistivity, which improves the signal to noise ratio. Additionally, high quality material in large volume is required for high gamma-ray interaction efficiency. Various compound semiconductor materials have been investigated for the potential use as a detector for room temperature gamma-ray spectroscopy. Table 2-1 shows the properties of a selection of these materials: gallium arsenide (GaAs), cadmium telluride (CdTe), cadmium zinc telluride ($\text{Cd}_{1-x}\text{Zn}_x\text{Te}$),
mercuric iodide (HgI₂), lead iodide (PbI₂), indium phosphate (InP), thallium bromide (TlBr), and bismuth iodide (BiI₃).

Table 2-1. Properties of selected compound semiconductor materials for room temperature gamma-ray spectroscopy.

<table>
<thead>
<tr>
<th>Detector Material</th>
<th>Atomic Numbers</th>
<th>Density (g/cm³)</th>
<th>Bandgap (eV)</th>
<th>Work Function (eV/e-h)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>31, 33</td>
<td>5.4</td>
<td>1.4</td>
<td>4.2</td>
<td>27-28</td>
</tr>
<tr>
<td>CdTe</td>
<td>48, 52</td>
<td>6.1</td>
<td>1.5</td>
<td>4.4</td>
<td>27-28</td>
</tr>
<tr>
<td>CdZnTe</td>
<td>48, 30, 52</td>
<td>6.1</td>
<td>1.6</td>
<td>4.7</td>
<td>28</td>
</tr>
<tr>
<td>HgI₂</td>
<td>80, 53</td>
<td>6.4</td>
<td>2.1</td>
<td>4.4</td>
<td>27-28</td>
</tr>
<tr>
<td>PbI₂</td>
<td>82, 53</td>
<td>6.2</td>
<td>2.6</td>
<td>4.9</td>
<td>28</td>
</tr>
<tr>
<td>InP</td>
<td>49, 15</td>
<td>4.8</td>
<td>1.4</td>
<td>4.2</td>
<td>28</td>
</tr>
<tr>
<td>TlBr</td>
<td>81, 53</td>
<td>7.6</td>
<td>2.7</td>
<td>6.5</td>
<td>28</td>
</tr>
<tr>
<td>BiI₃</td>
<td>83, 53</td>
<td>5.8</td>
<td>1.7</td>
<td>5.5</td>
<td>27</td>
</tr>
</tbody>
</table>

GaAs has been studied as a radiation detector since the early 1960s and was the first compound semiconductor material that clearly demonstrated good gamma-ray energy resolution at room temperature. GaAs crystallizes in a cubic, zincblende structure (space group $F43m$, No. 216) with four formula units per unit cell. GaAs has high charge carrier mobilities of 9000 cm²/Vs for electrons and 500 cm²/Vs for holes. The resistivity of GaAs crystal is on the order of $10^7 - 10^8$ Ω-cm, which is relatively low for a high resolution gamma-ray spectrometer. To reduce the leakage current, detector designs often employ Schottky barrier blocking contacts. GaAs has close atomic numbers to Ge, therefore the photoelectric absorption efficiency should be similar to Ge. High quality GaAs single crystals have been grown by liquid phase epitaxial (LPE) technique, but relatively small in volume and repeatability issues have prevented their commercial application. Attempts have been made to produce larger volume GaAs single crystals by bulk growth techniques such as vertical zone melt (VZM) and vertical gradient freeze (VGF). Unfortunately, charge trapping effects resulting from
the high impurity concentration have prevented the commercial realization of bulk GaAs as radiation spectrometers.\textsuperscript{34}

CdTe has been studied for room temperature gamma-ray detector since the mid-1960s.\textsuperscript{35-37} CdTe has the same crystal structure as GaAs (space group $F\overline{4}3m$, No. 216) with four formula units per unit cell. The charge carrier mobilities are 1000 cm$^2$/Vs for electrons and 80 cm$^2$/Vs for holes.\textsuperscript{38} The resistivity of CdTe crystal is on the order of $10^8 - 10^9$ Ω-cm.\textsuperscript{39} The photoelectric absorption efficiency is roughly a factor of 4 to 5 times higher than in Ge, and 100 times higher than in Si for typical gamma-ray energies. CdTe crystals have been grown using various techniques. Floating-zone melt growth has yielded crystals with low etch pit densities (EPD) on the order of $10^2$ cm$^{-2}$.\textsuperscript{40} The crystal rod has a moderate diameter of approximately 5 mm, primarily limited by the small surface tension and high density of the melt. The resistivity of the grown crystal was $10^6$ to $10^8$ Ω-cm. Variations of Bridgman growth methods (including vertical, horizontal, and high pressure) produced large ingots of CdTe.\textsuperscript{41-43} The resistivity was on the same order of magnitude as in the crystal grown by floating-zone. Crystals grown by these techniques are generally less suitable for gamma-ray spectrometers due to the inclusions of background impurities during the growth process.\textsuperscript{2} The traveling heater method (THM) is more commonly used to produce detector grade CdTe for several reasons including lower growth temperatures, reduced impurity concentrations, and lower defect concentrations than typical Bridgman methods.\textsuperscript{38} THM CdTe is often Cl doped to compensate background impurities and native defects, resulting in p-type material with high resistivity up to $10^9$ Ω-cm.\textsuperscript{44-45} Due to the poor hole mobility, energy resolution of CdTe detectors is generally not comparable with that of Si.
or Ge. The best energy resolution of CdTe detectors has been reported to be approximately 1.2% full width at half maximum (FWHM, 7.9 keV) for a $^{137}$Cs gamma-ray source (662 keV),\textsuperscript{46} while HPGe detectors can achieve 0.1% FWHM at 662 keV.\textsuperscript{47} Commercially available CdTe detectors have diameter ranging from 1 mm to over 1 cm, but charge trapping and non-uniformities in the electrical properties restrict detector thickness to a few millimeters or less. This makes CdTe detectors have less detection efficiency and poor spectroscopic performance for high-energy gamma-rays. Another drawback of CdTe detectors is polarization effect, which leads to a time-dependent decrease in the counting rate and charge collection efficiency.\textsuperscript{48} This polarization is largely related to the capture of electrons by acceptor type impurities within the material. The resulting space charge buildup counteracts the charge collection and decreases the depletion region of the detector.

The use of Cd$_{1-x}$Zn$_x$Te (CZT) crystals as gamma-ray detectors started around 1991.\textsuperscript{49} CZT has the same crystal structure as CdTe, with Zn substituting a fraction $x$ of the Cd atoms, where $x$ ranges from 0.04 to 0.2. The band gap energy at room temperature varies with Zn concentration, and is given by Olego \textit{et al.}\textsuperscript{50}

$$E_0(x) = 1.510 + 0.606x + 0.139x^2 \text{ eV}$$

in which the band gap energy of Cd$_{0.96}$Zn$_{0.04}$Te and Cd$_{0.8}$Zn$_{0.2}$Te are around 1.534 eV and 1.637 eV, respectively. The photoelectric absorption efficiency is similar to that of CdTe. The resistivity of CZT crystal is on the order of $10^{10} - 10^{11}$ $\Omega$-cm.\textsuperscript{51} The increased band gap reduces the intrinsic charge carrier concentrations. Furthermore, the operating leakage current is generally below that of CdTe devices due to the higher resistivity. The measured charge carrier mobilities are 1350 cm$^2$/Vs for electrons and 120 cm$^2$/Vs for holes.\textsuperscript{52} Similar to CdTe, the reported hole life time is much shorter than
the electron lifetime, which produces a condition in which position dependent charge collection can degrade energy resolution. High resistivity CZT is generally grown through the unseeded high-pressure vertical Bridgman (HPVB) technique. HPVB CZT ingots generally have high defect densities with reported EPD on the order of $10^4$ cm$^{-2}$. The defects can be metal inclusions, twins, grain boundaries, and in some cases severe polycrystallinity. Consequently, detector grade samples have to be painstakingly identified and separated from the bulk ingots, which increases the overall cost of the detectors. Despite the difficulties of obtaining high quality crystal samples, CZT detectors have shown significant improvement over CdTe in both size and spectrometric performance. The best energy resolution of CZT detectors has been reported to be of approximately 0.82% FWHM for a $^{137}$Cs gamma-ray source (662 keV). Unlike CdTe detectors, CZT detectors do not appear the phenomenon of polarization. CZT has become a very promising material for room temperature gamma-ray spectrometer and efforts to improve the crystal quality and detector performance are still ongoing.

HgI$_2$ has been investigated as a room temperature gamma-ray detector since the early 1970s. HgI$_2$ crystallizes in a tetragonal structure (space group P42/nmc, No. 137) at room temperature, appearing red color ($\alpha$ phase) with a band gap energy of 2.13 eV. The large band gap means this material has higher resistivity ($10^{12} - 10^{13}$ $\Omega$-cm) compared to CdTe or CZT. $\alpha$-HgI$_2$ has a layered structure with cleavage planes parallel to the (001) planes. It undergoes a phase transformation to an orthorhombic structure (space group Cmc21, No. 36) at 127°C, appearing a yellow color ($\beta$ phase) with a band gap of 2.5 eV. Because of this, HgI$_2$ detectors are usually operated in
environments with temperature below 127°C, and the detector material is always α-Hgl₂. The charge carrier mobilities of α-Hgl₂ are 100 cm²/Vs for electrons and 4 cm²/Vs for holes. The photoelectric absorption efficiency is much higher than CdTe and CZT detectors due to the higher atomic number of Hg (80), which means Hgl₂ detector can be relatively smaller for a required gamma-ray detection efficiency. For example, for 140 keV gamma-rays a 2 mm thick Hgl₂ detectors have comparable photoelectric absorption efficiency to a 4.2 mm thick CdTe or CZT detectors.² Due to the phase transformation, α-Hgl₂ single crystals cannot be grown from melt. Hgl₂ crystals were initially produced by solution growth technique.⁶² Radiation detectors fabricated from the solution grown material demonstrated some gamma-ray spectroscopic performance. However, crystals produced by this method are relatively small; impurity and solvent inclusions are commonly found in the grown crystal. Vapor phase processes including vertical and horizontal vapor growth are generally preferred for the growth of Hgl₂ crystals. Vapor phase methods allow the growth of large Hgl₂ crystals with high purity and low dislocation densities.⁶³-⁶⁵ Hgl₂ single crystals are generally collected from bulk crystals by cleaving samples perpendicular to the c-axis. For detector fabrication, samples are etched in a KI solution before the contacts are applied. The most commonly used contact materials are colloidal carbon (Aquadag) and Pd. The best energy resolution of Hgl₂ detectors has been reported to be approximately 0.93% FWHM for a ¹³⁷Cs gamma-ray source.⁶⁶ Hgl₂ has a high vapor pressure (5 x 10⁻⁵ torr) at room temperature; this will lead to a sublimation in air at a rate of 3 x 10⁻⁵ g/cm²-sec.⁶⁷ Therefore the material must be encapsulated with parylene⁶⁸ or a similar material to reduce the deterioration of the crystals over time. So far the development of
detectors from HgI\(_2\) largely remains at the research stage, mainly due to the problems associated with low hole mobilities, short charge carrier mean free path, space charge polarization, and surface degradation. Despite these operation difficulties, HgI\(_2\) is still a promising material for gamma-ray detectors because of the high detection efficiency, high density and high resistivity.

PbI\(_2\) remains interesting as an alternative semiconductor material for gamma-ray spectroscopy.\(^{69-71}\) The material crystallizes in a layered, hexagonal close-packed (HCP) structure (space group \(P\bar{3}m1\), No. 164) at room temperature.\(^{72}\) The reported charge carrier mobilities are 8 cm\(^2\)/Vs for electrons and 2 cm\(^2\)/Vs for holes.\(^{73}\) The low mobilities result in low energy resolution and detection efficiency, which prevent it from becoming a commercially viable semiconductor spectrometer. The relatively large band gap (2.55 eV) implies a high electrical resistivity (up to \(10^{13} \Omega\)-cm)\(^{74}\) and the device fabricated from this material can operate with low leakage current even at elevated temperatures. PbI\(_2\) crystals have been grown by vertical Bridgman,\(^{75}\) traveling molten zone (TMZ),\(^{76}\) and physical vapor deposition techniques.\(^{77}\) Similar to HgI\(_2\), single crystals of PbI\(_2\) can be cut from the bulk crystals along their cleavage planes (001). Crystal surfaces are polished and etched with KI solution before applying the contacts. The commonly used contact materials are Au, Pd, and Aquadag. Detectors fabricated from PbI\(_2\) was reported to have an energy resolution of 3% FWHM (1.83 keV) for 59.5 keV gamma-rays.\(^{78}\)

InP has been investigated as a possible gamma-ray spectrometer because its structural and electronic properties are similar to Si and GaAs, yet it has a higher photoelectric absorption coefficient. The crystal structure of InP is identical to GaAs.
The theoretical charge carrier mobilities are 4600 cm$^2$/Vs for electrons and 150 cm$^2$/Vs for holes. Single crystals of InP have been successfully grown by various techniques, including liquid encapsulated Czochralski (LEC), horizontal and vertical Bridgman, vertical gradient freeze (VGF), and synthesis solute diffusion (SSD) method. However, the quality and size of grown InP crystals are still far below the requirement for a good gamma-ray spectrometer. Charge trapping remains a persistent problem for this material. Development work still continues in the hope of producing better quality crystals.

TlBr crystals have drawn great interest as an alternative material for room temperature gamma-ray spectrometers due to their high atomic number, high density, and large band gap. These favorable properties potentially yield a gamma-ray detector with compact size and high detection efficiency. The crystal structure of TlBr is simple cubic CsCl-type (space group $Pm\overline{3}m$, No. 221). Since all thallium compounds are toxic, this material requires extremely precautions during handling and use. TlBr has poor charge carrier mobilities of 30 cm$^2$/Vs for electrons and 4 cm$^2$/Vs for holes, which limit it from being commercialized. Single crystals of TlBr have mainly been grown by either the vertical Bridgman or Bridgman-Stockbarger technique. Similar to other currently researched materials, poor crystal quality and charge trapping issues require further study of this material before commercialization.

Bi$I_3$, which is the main focus of this work, has been studied as a room temperature gamma-ray detector since the mid-1990s. The development of this material is rather slow, mainly due to the difficulties of producing large and high quality crystals. With recent progress on material purification, Bi$I_3$ single crystal platelets have been
grown by physical vapor deposition (PVD). They have shown response to X-rays, yet the crystal was small in volume therefore no spectra was collected.\textsuperscript{9,13} The theoretical charge carrier mobilities are 680 cm\textsuperscript{2}/Vs for electrons and 20 cm\textsuperscript{2}/Vs for holes.\textsuperscript{90} Similar to \(\alpha\)-Hgl\(_2\), BiI\(_3\) has a layered structure with cleavage planes perpendicular to [001] direction. With similar high atomic number, high density, and large band gap to Hgl\(_2\), BiI\(_3\) should have comparable radiation performance to Hgl\(_2\) if detector grade material can be produced.

Other semiconductor materials have been studied with limited success, including CdSe,\textsuperscript{91} GaSe,\textsuperscript{92} cubic boron phosphide (BP),\textsuperscript{93} AlSb,\textsuperscript{94} CdS,\textsuperscript{95} ZnSe,\textsuperscript{96} and SiC.\textsuperscript{97} Most of these materials are limited to the high concentrations of impurities and traps, and they are generally not commercially available.

### 2.3 Physical Properties of BiI\(_3\)

BiI\(_3\) crystallizes in a rhombohedral structure (space group \(R\bar{3}\), No. 148) with six formula units per unit cell. The lattice parameters of BiI\(_3\) are \(a = 7.519 \text{ Å}\) and \(c = 20.720 \text{ Å}\).\textsuperscript{10} Within the lattice, the Bi\(^{3+}\) ions occupy the 6c Wyckoff positions with coordinates (0, 0, 0.1693), while the I\(^-\) ions reside in the 18f positions with coordinates (0.3322, 0.3146, 0.0797).\textsuperscript{98} A schematic representation of the BiI\(_3\) crystal structure is presented in Figure 2-4. It can be seen from Figure 2-4a that BiI\(_3\) adopts a layered structure with Bi\(^{3+}\) ions establishing a six-fold coordination with I\(^-\) ions. Also, the I\(^-\) ions establish a non-linear two-fold coordination with I\(^-\) ions. Also, the I\(^-\) ions establish a non-linear two-fold coordination with I\(^-\) ions. Each unit cell consists of three I-Bi-I layers stacked along [001] direction, and within each I-Bi-I layer three close-packed atomic sheets stack in the sequence of I-Bi-I. The sites in I sheets are fully occupied, while only two thirds of the sites in the Bi sheets are occupied, as shown
in Figure 2-4b. There are three different ways of Bi sites occupation in the close-packed array. In the normal stacking, the three different layers are successively stacked along the c axis in the sequence of $\alpha\beta\gamma\alpha\beta\gamma\alpha\beta\gamma\cdots$, where $\alpha$, $\beta$, and $\gamma$ denote the three possible positions of the close-packed I-sheet, and A, B and C the three Bi-sheets. Stacking of the layers is rarely perfect, therefore stacking faults are commonly found in Bil$_3$ crystal. Furthermore, based on the electronic structure of Bil$_3$, the Bi-I bonds are highly ionic with the 3 p-electrons of bismuth lost to iodine. The I-Bi-I layers are held together by weak van der Waals forces. Thus Bil$_3$ crystal can be easily cleaved along [00l] direction. On the other hand, the weak van der Waals bonding makes this material soft and difficult to handle. The anisotropic crystallography of this material indicates the anisotropy of various physical properties such as electrical and thermal conductivity. This special crystal structure also determines a preferred growth along the (00l) planes during crystal growth.

(a) (b)

Figure 2-4. Hexagonal representation of Bil$_3$ crystal structure, a) unit cell consists of three I-Bi-I layers; b) projection of one I-Bi-I layer indicating missing Bi sites. Smaller Bi$^{3+}$ ions appearing in blue, while the larger I- ions are presented in red. The dashed box represents one unit cell.
The layered structure of BiI₃ leads to a quasi two-dimensional characteristic of excitons in BiI₃, which makes it an attractive material for nonlinear optics. An exciton is a quasiparticle consisting of an electron and a virtual particle called an electron hole with a bound state in insulators and semiconductors. An exciton is formed when a photon enters a semiconductor, exciting an electron from the valence band into the conduction band, leaving a localized hole of opposite electric charge behind, to which the electron is attracted by the Coulomb force. Exciton states in BiI₃ are observed near the fundamental absorption edge and characterized by a small Bohr radius (~ 6 Å) of about the unit cell size. Excitonic transitions have been described by a model on the basis of the excitation from s to p electronic states in the cation Bi. The model has been confirmed by the studies of the magneto-optical spectra under strong magnetic field. The exciton motions in BiI₃ have been well studied near the band edge transitions by optical techniques. As shown in Figure 2-5, the optical absorption edge of BiI₃ starts as an indirect exciton transition assisted by three different momentum conserving phonons, named A, B, and C. The indirect exciton transition (Eᵢₓ = 2.0081 eV at 2 K, gx = exciton ground state) occurs at slightly lower energy to the direct exciton energy (Eᵈᵢₓ = 2.072 eV) and subsequently exhibits an extraordinarily large oscillator strength.

In addition, a series of sharp sample-dependent absorption lines can be observed below the indirect exciton lines at liquid helium temperature. They are labeled as P, Q, R, S, and T from the higher energy side. The P line appears very close to the indirect exciton energy and it does not always appear together with Q, R, S, and T lines, which...
suggests that the origin of the P line is different from the others. It has been suggested by Kaifu et al. that the P line is associated with the polytypic stacking disorder.\textsuperscript{107} The Q, R, S, and T lines were initially ascribed to the formation of a bielectron (or bihole) by Gross and his co-workers.\textsuperscript{115} However, since the appearance and the intensities of these lines vary with the respective samples, they should be attributed to some defects in origin; also various difficulties in the bielectron model have been pointed out.\textsuperscript{116-119} The appearance of R, S, and T lines was later attributed to excitonic transitions perturbed by a stacking fault that occurred between unit layers.\textsuperscript{114} The stacking fault distorts the unit cell symmetry and creates new exciton states near the stacking fault plane. On the stacking fault plane, a new translational symmetry is constructed, which allows a quasi two-dimensional motion for the excitons. These excitons bind at the stacking fault and are called the stacking fault excitons (SFE). The model based on the stacking fault has been confirmed by the magneto-optical studies, resonant Raman scattering, and space-resolved optical measurements.\textsuperscript{109,114,120} The absorption coefficients of the R, S, and T lines vary from sample to sample, but the intensity ratios among them are nearly constant and are about 4:2:1, which has been explained as reflecting the degeneracy of the SFE levels.\textsuperscript{114} Exciton propagation along the stacking fault plane has very high efficiency and coherent characters since they have small radius and are less scattered by phonons.

There is no significant dissociation reported for BiI\textsubscript{3} at temperature below 600\textdegree C. However, a study by Cubicciotti and Keneshea suggested that BiI\textsubscript{3} tends toward dissociation into Bi and I\textsubscript{2} at 250 – 300\textdegree C,\textsuperscript{5} although only by a few percent. This
tendency will lead to a distortion of stoichiometry and result in the deteriorate properties of the material.\textsuperscript{13}

The other properties of BiI\textsubscript{3} will be discussed in the following chapters. Chapter 3 will cover the chemical and mechanical properties including stability, hardness, and resistance to etchant. Chapter 4 will discuss the optical properties and band gap of BiI\textsubscript{3}. Chapter 5 will discuss the electrical properties of BiI\textsubscript{3}.

![Absorption Spectrum](image)

Figure 2-5. The absorption spectrum near the indirect edge and its stacking disorder effect.\textsuperscript{110}

### 2.4 Thermodynamics of Crystal Growth from Melt

This section discusses the general thermodynamics of crystal growth. The whole discussion is based on chapter 7 in Solidification by Dantzig and Rappaz.\textsuperscript{121} An in depth discussion on the vertical Bridgman crystal growth will be given in chapter 3 in this dissertation.
2.4.1 Nucleation

The crystal growth process begins with the creation of small clusters of atoms with crystalline structure when the temperature is below the material’s melting point. Most of the clusters will repeatedly come together and fall apart. Some clusters may by chance grow larger than a critical size. Once the cluster exceeds this critical size, it can continue to grow and eventually form large crystals. The process to create a sufficiently large and stable cluster is called nucleation. There are two classes of nucleation processes: homogeneous and heterogeneous nucleation. Homogeneous nucleation involves the spontaneous formation and subsequent growth of small particles of the new phase. Heterogeneous nucleation begins on a foreign material such as a particle or a surface. Heterogeneous nucleation has a smaller energy barrier to overcome, therefore most nucleation processes in the real world are heterogeneous. The driving force for the nucleation is the Gibbs free energy difference of the two phases, which is caused by the undercooling of the melt.

2.4.1.1 Homogeneous Nucleation

Consider a simple case of formation of solid nuclei in the melt of a liquid phase, the change in Gibbs free energy upon the formation of a cluster of atoms can be described by two contributions, one from the decreased free energy associated with the formation of the new phase, and the other from the surface tension of the small cluster. Assuming that the cluster has a sphere shape with radius \( r \), the change in Gibbs free energy can be written as

\[
\Delta G_{\text{hom}} = -\frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \sigma
\]  

(2-4)
where $\Delta G_v$ is the difference in free energy per unit volume between the liquid and solid phase, and $\sigma$ is the specific surface free energy. The critical size $r^*$ of the cluster can be determined by

$$\frac{\partial \Delta G_{\text{hom},v}}{\partial r} = -4\pi r^2 \Delta G_v + 8\pi r \sigma = 0$$  \hspace{1cm} (2-5)$$

which gives the critical radius

$$r^* = \frac{2\sigma}{\Delta G_v}$$  \hspace{1cm} (2-6)$$

A cluster that is below the critical size is called an embryo. If it reaches critical size, it becomes a nucleus. The Gibbs free energy to form a nucleus is then given by

$$\Delta G^*_v = \frac{16}{3} \pi \sigma^3 \frac{\Delta G_v^2}{\Delta G_v}$$  \hspace{1cm} (2-7)$$

Equation (2-7) gives the height of the energy barrier which should be overcome for homogeneous nucleation to occur. For a liquid that is supercooled below its melting point, we can write

$$\Delta G_v = \frac{L \Delta T}{T_m}$$  \hspace{1cm} (2-8)$$

where $\Delta T$ is the undercooling, $L$ is the latent heat, and $T_m$ is the melting point. Substituting equation (2-8) in equation (2-7) yields

$$\Delta G^*_{\text{hom},v} = \frac{16}{3} \pi \sigma^3 \frac{T_m^2}{L^2 \Delta T^2}$$  \hspace{1cm} (2-9)$$

Equation (2-9) indicates that the energy barrier to formation of a critical nucleus decreases rapidly with increasing undercooling $\Delta T$. A large undercooling is therefore essential for the homogeneous nucleation.

**2.4.1.2 Heterogeneous Nucleation**

As previously stated, most nucleation processes are not homogeneous. Nucleation will prefer to occur on impurity particles, ions or foreign surfaces first due to
the smaller energy barrier. Considering the case of nucleation on a foreign surface as shown in Figure 2-6, the embryo is assumed to take the shape of a spherical cap. The wetting angle $\theta$ is determined by the balance of the three surface energies between the solid, liquid, and foreign surface.

![Figure 2-6. The nucleation of a spherical solid cap at a liquid-substrate interface.](image)

The equilibrium condition can be expressed by the well known Laplace-Young equation

$$
\sigma_{fl} = \sigma_{fs} + \sigma_{sl} \cos \theta \quad \text{(2-10)}
$$

where the two subscripts on the surface energies indicate the two substances in contact, namely s for solid and l for liquid, and f represents the foreign substrate. The change of the Gibbs free energy upon formation of the embryo is given by

$$
\Delta G_{hot} = -V \Delta G_v + \Phi \quad \text{(2-11)}
$$

where $V$ and $\Phi$ are the volume and surface energy of the embryo, respectively. They are given by

$$
V = \frac{4}{3} \pi r^3 \left(1 - \cos \theta\right)^2 \left(2 + \cos \theta\right) \quad \text{(2-12)}
$$

$$
\Phi = 2\pi r^2 \left(1 - \cos \theta\right) \sigma_{sl} + \pi r^2 \sin^2 \theta \left(\sigma_{fs} - \sigma_{fl}\right) \quad \text{(2-13)}
$$

by solving equation (2-10) through (2-13), we get
\[
\Delta G_{\text{het}} = \left(-\frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \sigma_{sl}\right) f(\theta) = \Delta G_{\text{homo}} f(\theta) \quad (2-14)
\]

\[
f(\theta) = \frac{V}{4 \pi r^3 / 3} = \frac{(1 - \cos \theta)^2 (2 + \cos \theta)}{4} \quad (2-15)
\]

where \( f(\theta) \) is a geometric factor given by the ratio of the volume of the spherical cap and a full sphere of identical radius. Equation (2-14) reveals that the Gibbs free energy change for heterogeneous nucleation has the same form as for homogeneous one, but is multiplied by \( f(\theta) \). Following the same procedure as before, the critical radius gives exactly the same result as for the homogeneous nucleation

\[
r^* = \frac{2\sigma}{\Delta G_v} = \frac{2\sigma T_m}{L \Delta T} \quad (2-16)
\]

The energy barrier for heterogeneous nucleation is then determined to be

\[
\Delta G^*_{\text{het}} = \frac{16}{3} \pi \sigma^3 \Delta G^2_v \frac{f(\theta)}{\Delta G_v} = \frac{16}{3} \pi \sigma^3 T_m^2 \frac{f(\theta)}{L \Delta T} = \Delta G^*_{\text{homo}} f(\theta) \quad (2-17)
\]

The nature of the heterogeneous nucleation is determined by the function \( f(\theta) \). When \( \theta = \pi \), \( f(\theta) = 1 \), which corresponds to a complete non-wetting of the solid on the substrate. This case is equivalent to homogeneous nucleation. When \( \theta = \pi / 2 \), \( f(\theta) = 1 / 2 \), and \( \sigma_{fl} = \sigma_{fs} \). In this case, the cap forms a hemisphere. Although there is no surface energy reduction when the solid embryo forms on the substrate, the presence of the substrate reduces the nucleation energy barrier required to form a critical nucleus by half. When \( \theta = 0 \), \( f(\theta) = 0 \), corresponding to a perfect wetting of the solid phase on the substrate. An example is when the solid itself is the substrate, there is clearly no nucleation barrier and solidification is limited only by growth. This case is equivalent to crystal growth on a seed. In summary, whenever easily wetted foreign particles are present in the melt, they induce heterogeneous nucleation under normal cooling conditions. The required undercooling for heterogeneous nucleation is much smaller than that for homogeneous nucleation.
2.4.2 Nucleation Rate

A nucleus with critical size \( r^* \) will grow if it manages to add one more atom. The rate at which this occurs is proportional to the atomic vibration frequency \( \nu_0 \) and the probability of capturing an atom at the surface \( p_c \). Thus, the nucleation rate is given by

\[
I = \nu_0 p_c n_i^* = \nu_0 p_c n_0 \exp(-\frac{\Delta G^*}{kT}) = \nu_0 p_c n_0 \exp\left(-\frac{16 \pi \sigma^2 T_m^2}{3 L^2 \Delta T^2 kT} f(\theta) \right)
\]  

(2-18)

where \( n_i^* \) is the number of critical nuclei per unit volume, \( \Delta G^* \) is the energy barrier to nucleation, \( n_0 \) is the density of atoms in the liquid for homogeneous nucleation, or density of the heterogeneous nucleation sites in the liquid for heterogeneous nucleation. For homogeneous nucleation, \( f(\theta) = 1 \).

The nucleation rate strongly depends on temperature through two competing phenomena as denominated in the exponential in equation (2-18). A large undercooling \( \Delta T \) tends to increase the nucleation rate, while the low temperature decreases the mobility of atoms thus decreases the nucleation rate. The competition between these two phenomena results in the appearance of the maximum nucleation rate at a compromised undercooling.

2.4.3 The Crystal Growth Face

Once the nucleation is complete, it is immediately followed by growth stage in which atoms in the melt attach themselves to the solid-liquid interface. There are two different types of interface structures: atomically rough or smooth interface. In the atomically rough interface, the transition from liquid to solid takes place over a number of atomic layers. With increasing distance into the interface, the thermodynamic properties of the atoms within the layers vary continuously from those of the liquid to
those of the solid. In the atomically smooth interface, the transition from liquid to solid ideally takes place across a single atomic layer.

The earliest theoretical predictions on the interface structures were made by Burton et al., who demonstrated that the interface would be rough at the growth temperature for most metal crystals. Jackson pointed out that the equilibrium interface structure is in equilibrium with both the crystal and the melt. He assumes that atoms are randomly placed on a surface that was initially atomically smooth, and calculates the change in surface free energy as follows:

$$\Delta G = RT_m [\alpha x (1-x) - x \ln x - (1-x) \ln (1-x)]$$

(2-19)

where $R$ is the gas constant, $T_m$ is the melting temperature, $x$ is the occupation fraction of the surface sites, and $\alpha$ is called the Jackson alpha factor, which is defined as:

$$\alpha = \frac{L}{kT_m} \frac{u}{w}$$

(2-20)

where $L$ is the heat of fusion, $k$ is the Boltzmann constant, $u$ and $w$ are the nearest neighbors of an atom on the surface and inside the solid respectively. The fraction $u/w$ gives a measure of the binding force. In particular, if a cut is made through a crystal leaving a surface described by $u$ and $w$, the free energy of the surface is proportional to $(1-u/w)$.

Equation (2-19) gives a relationship between the change of free energy $\Delta G$, the fraction of sites filled $x$, and the Jackson alpha factor. Figure 2-7 shows the results of Jackson’s calculation. For materials with $\alpha < 2$, there is a broad minimum at $x = 0.5$, indicating that the interface energetically prefers to be atomically rough. On the other hand, in a material with $\alpha > 2$, there are two minima at $x \to 0$ and $x \to 1$. These minima approach the limiting $x$ values (0 and 1) and become sharper as $\alpha$ increases. The two
minima indicate that either very few sites are filled on a complete surface or almost all sites are filled. Both conditions describe a smooth interface.

![Figure 2-7. Variation of free energy of interface with fraction of sites filled.](image)

The $\alpha$ factors are different for different materials. Metal crystals generally have $\alpha < 2$; semiconductor crystals have $2 < \alpha < 3$; and oxides, silicates, and polymer crystals, which have complicated crystal structures, have $\alpha > 3$. Due to the presence of u/w, the $\alpha$ factors will also be different in different crystallographic directions in the same crystal.

### 2.5 BiI$_3$ as a Radiation Detector

BiI$_3$ may allow one to efficiently detect and discriminate medium and high-energy gamma-rays. The high effective atomic number yields a detector that has a relatively high photoelectric cross-section for moderate and high energy gamma-rays. Theoretical modeling of intrinsic photopeak efficiency has been performed to compare BiI$_3$ to HgI$_2$, PbI$_2$ and CZT by Azaree et al. The modeling was conducted by using the Los Alamos developed Monte Carlo N-Particle (MCNP) code. MCNP generates
results based on the probability of physical interactions occurring. The probability of interaction occurrence is determined through the use of data libraries that are built into the software package. The geometry for the simulations with each of the materials was kept the same. The data was generated by modeling a one cubic centimeter detector located a distance of one centimeter from a square centimeter surface source. Ten million photons were started, which negated the need for any variance reduction to be performed. The number of photons that yielded a total energy deposition was obtained for energies ranging from the zero to 3 MeV at intervals of 5 keV. It is evidenced in Figure 2-8 that the peak efficiency for BiI₃ is comparable to HgI₂ and PbI₂, and a factor of two higher than CdZnTe. For example, the intrinsic photopeak efficiency for BiI₃ is approximately 20%, while CdZnTe is 10% for a 662 keV gamma-ray. The wide bandgap of BiI₃ will allow for room temperature operation and harsher temperature environments may be possible.

![Graph showing intrinsic photopeak efficiency as a function of energy for 1 cm³ detectors located 1 cm from a surface source. Re-plotted after Lintereur et al.](image)

Figure 2-8. Intrinsic photopeak efficiency as a function of energy for 1 cm³ detectors located 1 cm from a surface source. Re-plotted after Lintereur et al.¹²⁷

Although BiI₃ has been studied for over a century, the attempt to use it as a radiation detector only started in 1990s. Nason and Kellor were the first researchers to
test the radiation response of BiI₃ single crystal. The single crystals were grown by the PVT method with a seed obtained via the sublimation of commercial BiI₃ powder. The largest single crystal they obtained has a dimension of 1.2 x 1.2 x 0.4 cm³. The detectors were fabricated by applying colloidal graphite electrodes and connected with Pd wire. The resistivity was reported to be (2 - 5) x 10⁹ Ω·cm. However, they were unable to collect any signal from 60 keV gamma-ray or 5 MeV α-particle irradiation, mainly due to the poor crystal quality.

Following their work, Dmitriev et al. grew BiI₃ single crystal by the vertical Bridgman method directly from commercially available powder (99.999% purity). The detectors were fabricated by applying vacuum-evaporated Pd electrode and attached with Pd wire using silver epoxy. The resistivities of the crystals were measured to be (0.5 - 2) x 10⁹ Ω·cm. By applying AC coupling on the detector, they successfully observed the detector response to pulse X-ray excitation. However, spectrum relationship could not be established due to polarization effects, which were related to the defect structure in the crystal.

In 2002, Matsumoto et al. fabricated a better detector from BiI₃ crystals grown by the vertical Bridgman method. Electrodes with 1 mm in diameter were deposited by vacuum evaporation of Pd on the surface, and Pd wires were bonded to the Pd electrodes using silver epoxy. The resistivity of a 82 μm detector was measured at 1.7 x 10¹⁰ Ω·cm. Although this detector exhibited a clear peak response to a ²⁴¹Am α-particle source (5.48 MeV), the energy resolution was rather poor with 40% FWHM (2.2 MeV). The detector was not able to obtain any spectra from X-ray and gamma-ray sources.
Different from the approach using bulk crystals, Fornaro et al. focused their work on \( \text{BiI}_3 \) platelets\textsuperscript{13} and thin film\textsuperscript{128} with the application towards X-ray detection. The platelets were grown by the PVT method with an average dimension of \((100 – 200) \text{ mm}^2 \times (50 – 80) \mu \text{m}\). Both Pd and Au were tested as electrodes for the detector. The Au electrode gave the higher resistivity values about \(0.6 \times 10^{12} \ \Omega \cdot \text{cm}\) higher than that of detector with Pd electrode. The resistivities, as high as \(2 \times 10^{12} \ \Omega \cdot \text{cm}\), were obtained and were 2 orders higher than that of the bulk crystal. However, the detectors only showed response to a \(^{241}\text{Am} \alpha\)-particle source and no X-ray spectra were collected. \( \text{BiI}_3 \) polycrystalline film was grown by the PVT method on a 1” x 1” glass substrate. The glass substrate was initially deposited with Pd electrode as rear contact by thermal evaporation. After film growth, Pd electrode with area of 4 mm\(^2\) was deposited as the front contact. The measured resistivity of the polycrystalline film was relatively high with values up to \(6 \times 10^{12} \ \Omega \cdot \text{cm}\). Detectors fabricated from the films showed significant response to a \(^{241}\text{Am} \) source, and the current density was observed to increase linearly with increasing exposure time under an X-ray beam of several kilovoltages.

Previous efforts of pushing \( \text{BiI}_3 \) as a room temperature radiation detector were very encouraging. Similar to the development of CZT and Hgl\(_2\) detectors, the success of the detector is largely determined by the crystal quality.\textsuperscript{3,129} Therefore, this study investigated the growth conditions of \( \text{BiI}_3 \) single crystal using a modified vertical Bridgman method. The dependence of crystal quality on the growth conditions has been investigated using various characterization techniques, which will be discussed in detail in chapter 3. The preliminary results will provide a guideline for a future crystal grower to have a better control on the qualities of \( \text{BiI}_3 \) single crystals.
3.1 Introduction

As discussed in Chapter 2, the crystal growth techniques for BiI$_3$ can be summarized as vertical Bridgman and PVT. While the PVT method can produce high quality but small volume crystals, the vertical Bridgman technique can grow crystals with larger volume but the crystal quality is not as good as those grown from PVT.$^{11-13,130}$ This chapter discusses the growth of BiI$_3$ single crystals using the modified vertical Bridgman (MVB) technique. The quality of the crystals grown under different conditions was evaluated and compared to that of crystals grown by PVT method.

3.2 Crystal Growth Techniques of BiI$_3$

3.2.1 Vertical Bridgman Technique

As the name says, this technique is named after P. W. Bridgman who is the first one using this method to grow a series of metal single crystals.$^{131}$ The principle of this technique involves lowering a crucible through a furnace so that the freezing starts at the lowest point in the crucible and the solidification interface slowly moves up along the crucible. The movement rates for such processes range from around 0.1 to 200 mm/h.$^{124}$ A typical vertical Bridgman system is shown in Figure 3-1. The movement of the crucible is controlled by a dropping motor. A longitudinal temperature profile is established at the center of the furnace with specific temperature gradient near the melting point of the material. The hole in the lid should be small and the lid should fit well with the furnace body to prevent thermal disturbance.
The crystal growth with vertical Bridgman method can use a seed or no seed. A non-seeded Bridgman method relies on random nucleation to produce a single crystal which then propagates to form one large crystal through the whole frozen charge. The formation of just one nucleus requires a small nucleation volume. Thus the crucibles are normally shaped with sharp tips to meet the nucleation criteria, as illustrated in Figure 3-1(a). For a seeded Bridgman growth, the crucible shape is not that important. Normally a flattened bottom is made to accommodate the seed material. The most obvious requirement for a crucible is that it should not react with the crystals within the temperature range of crystal growth. It also should have a smaller coefficient of thermal expansion than the crystal to avoid the induced strain and stress during cooling.
For vertical Bridgman crystal growth, the quality of the single crystal is largely determined by the control of heat flow during crystallization. The thermal conditions of a practical crystal growth system are rather complicated, thus analytical solutions are not possible without simplifications and assumptions. In the following discussion, it is assumed that the melt is a single component material, the density of the melt and its crystal are the same, temperature gradients within the crystal transverse to the growth direction are negligible, and the solid-liquid interface is planar. During crystal growth, a heat balance is set up by the conservation of heat flux at the interface, which can be written as

\[ \rho_s L R = K_s G_s - K_L G_L \]  

(3-21)

where \( K_s \) and \( K_L \) are the thermal conductivity of solid and liquid (cal/(cm·°C·s)), \( G_s \) and \( G_L \) are the temperature gradient in solid and liquid at the solid-liquid interface (°C/cm), \( \rho_s \) is the density of solid (g/cm³), \( L \) is the latent heat of melt (cal/g), and \( R \) is the growth rate (cm/s). The left side in Equation (3-1) indicates the heat generated at the interface due to solidification. The first term on the right side is the heat flux going out of the solid-liquid interface. The second term on the right side refers to the heat flux coming into the solid-liquid interface. Equation (3-1) indicates that the growth rate \( R \) can be controlled by independently adjusting \( G_s \) and \( G_L \). This is important as growing good single crystals requires that the temperature gradient be high and growth rate be low. The temperature gradient in liquid (\( G_L \)) is directly proportional to the heat flux in the liquid at the solid-liquid interface. The temperature gradient in solid (\( G_s \)) is normally determined empirically or through heat flow calculations. In a cylindrical system, the heat conduction in solid can be described as.
\[
\frac{\partial}{\partial z} \left[ K_s \frac{\partial T}{\partial z} \right] = \rho_s c_s \left[ \frac{\partial T}{\partial t} + R \frac{\partial T}{\partial z} \right]
\]  
(3-22)

where \( c_s \) is the specific heat of solid (cal/(g·°C)), and \( z \) is the coordinate parallel to the growth direction. Physically, the term on the left represents the net rate of heat conduction away from the solid per unit volume. The first term on the right side represents the decrease rate of internal energy per unit volume. The second term on the right side is the rate of energy released per unit volume due to interface moving.

Some simplifications need to be made to solve equation (3-2). For example, in the case of floating zone (crucibleless) growth, assuming the crystal has a cylindrical shape, temperature gradients along the transverse direction are negligible, and heat transfer from the crystal to surrounding is by convection. At steady state, the temperature gradient in solid at the solid-liquid interface is given by

\[
G_s = (T_m - T_0) \left[ \left( \frac{R}{2\alpha_s} \right)^2 + \frac{2h}{rK_s} - \frac{R}{2\alpha_s} \right]
\]  
(3-23)

where \( T_0 \) is the ambient temperature (°C), \( T_m \) is the melting point of the crystal, \( \alpha_s \) is the thermal diffusivity of the solid crystal (Ks/\( \rho_s c_s \), cm²/s), \( h \) is the heat transfer coefficient from solid to ambient (cal/(cm²·°C·s)), and \( r \) is the radius of crystal (cm). Since the growth rate \( R \) is usually small, when \( R/2\alpha_s \ll 1 \), equation (3-3) becomes

\[
G_s \approx (T_m - T_0)(2h/rK_s)^{1/2}
\]  
(3-24)

For crystals with high melting point, \( (T_m - T_0) \) is large and the heat transfer coefficient \( h \) is increased by radiation heat transfer. The attainable \( G_s \) can be as high as 100°C/cm or more. For low melting point crystals, external cooling has to be applied to achieve steep gradients.

It should be noted that the analytical solutions cannot completely explain and predict the crystal growth in a practical vertical Bridgman system. This is mainly
because the simplifying assumptions usually tend to discard some important details which control crystal growth.\textsuperscript{134-135} Accordingly, numerical studies have been performed to gain more understandings in the vertical Bridgman growth process.\textsuperscript{82,132,136-142} Studies have been focused on controlling the solid-melt interface shape,\textsuperscript{82,137} models of the heat and mass transfer,\textsuperscript{138-139,142} and the influence of the thermal environment and process parameters.\textsuperscript{140-141} Accurate material thermal properties and operating environment are required for successful numerical predictions.

### 3.2.2 Physical Vapor Transportation Technique

The crystal growth by the PVT method is typically conducted in closed or semi-closed systems. If the vapor pressure of a material at a desired growth temperature exceeds $10^{-2}$ torr, it may be efficiently grown by the PVT method.\textsuperscript{143} In the PVT process, an ampoule containing a polycrystalline source of the desired material is heated to a temperature at which the material starts to sublime at a rate leading to crystal growth. The ampoule is typically placed in a furnace that provides a temperature gradient over the length of the ampoule, so that the polycrystalline source material sublimes at the higher temperature and deposits at the end of the ampoule where the temperature is lower. This temperature difference causes the different vapor pressure at two ends of the ampoule and forces the material transport from the source to the cooler end. The PVT system can adopt horizontal or vertical set up. A typical horizontal PVT system is illustrated in Figure 3-2.

For crystal growth by PVT method, the growth temperature $T_2$ should exceed about one-third of the melting temperature of the crystal.\textsuperscript{124} The temperature $T_1$ is fixed so that the crystal grows at an acceptable rate which can be deduced from simple theory as follow. The vapor pressure can be expressed in the form of
\[ P = P_0 \exp\left(\frac{-\Delta H_s}{RT}\right) \]  

then the rate of deposition in an ideal case with an evacuated ampoule is\textsuperscript{124}

\[ f = P_0 \left[ \exp\left(\frac{-\Delta H_{s1}}{RT_1}\right) - \exp\left(\frac{-\Delta H_{s2}}{RT_2}\right) \right] \left(\frac{M}{2\pi RT_2}\right)^{1/2} \rho \]  

(3-26)

Figure 3-2. Schematic diagram of physical vapor transport (PVT) system. Diagram after Isshiki and Wang.\textsuperscript{144}

where \( \Delta H_s \) is the latent heat associated with the vaporization of a solid below its melting point (cal/g), \( \rho \) is the density of the crystal (g/cm\(^3\)), \( M \) is the molecular weight of the vapor (g/mole), and \( R \) is the gas constant (cal/(K·mole)). Equation (3-6) indicates that the growth rate of PVT method can be controlled by adjusting the temperature difference at two ends of the ampoule. Normally inert gases (N\(_2\), Ar) are infused into the ampoule after vacuum treatment to assist the nucleation of PVT crystal growth.\textsuperscript{9,129,145} Since PVT growth is carried out at temperature much lower than the melting point of the material, it has multiple benefits of:\textsuperscript{126} (a) reduced diffusion of impurities from containers, (b) reduced defects such as voids and dislocation densities, and (c) effective separation of impurities with low vapor pressure during transport. The major drawbacks for PVT methods are small crystal volume and uncontrolled
nucleation. In practice, unless there is a large temperature gradient near the cooler end of the ampoule, multiple nucleations occur and the products at the cooler end are needles, platelets, or polycrystalline formed by many small crystals.

3.3 Experimental Procedures

3.3.1 Modified Vertical Bridgman Growth

In this study, BiI₃ single crystals were mainly grown by a modified vertical Bridgman method. Pyrex glass ampoules were selected as the crystal growth containers since the annealing and softening points of the glass are 560°C and 815°C respectively, which are much higher than the maximum temperature (440°C) used in the growth of BiI₃ single crystal. The Pyrex glass tube was soaked in Decon Contrad® 70 for 12 hours to effectively remove the organics, rinsed 10 times with high purity DI water ($\rho = 13.6$ MΩ-cm) and baked at 120°C for 12 hours. One end of the cleaned glass tube was melted and shaped to a sharp tip using a propane hand torch. BiI₃ powder (99.999%, MV Laboratories) was weighed and loaded in this tipped Pyrex glass ampoule. The ampoule needs to be evacuated and sealed to get rid of the water and oxygen as BiI₃ will react with them at elevated temperature. To do that, the ampoule was first vacuumed to a pressure of approximately $4 \times 10^{-6}$ mbar. Heat was then gently applied on the ampoule wall using a propane hand torch to help evaporate the water. This step has to be done very carefully to avoid heating up the BiI₃ powder. Ar gas was then back filled in the ampoule to ~700 mbar. The purpose of infusing Ar gas is to make sure any residual gas after vacuum is inert. The cycle of pumping down, heating ampoule wall, and backfilling Ar gas was repeated three times, the final evacuation took around another 2-3 hours to take the pressure down to $10^{-6}$ mbar. The ampoule was then sealed using a propane hand torch. To help seal the ampoule, a neck area was
preformed in air before the ampoule was pumped down. As the soft glass will collapse inwards due to the inner vacuum, the neck area will help the glass collapse into the opposing wall without breaking the seal. After sealing, the ampoule was vertically fixed in a standing frame and placed in a programmable 24 heating zone furnace (EDG-13, Mellen Company). The length of each heating zone is one inch and the temperature of each heating zone can be independently controlled by a computer program, which allows a precisely controlled temperature profile along the vertical axis of the furnace. The powder was first heated and kept at 440°C for 24 hours then cooled to 420°C at a rate of 10°C/h. The temperature profile was programmed to move up along the vertical axis with a fixed rate. This simulated the downwards movement of the ampoule in the conventional vertical Bridgman method. The set up of this modified Bridgman system provides two advantages over the conventional one. First, possible vibration during crystal growth is eliminated since the ampoule is kept static in the new system. Second, a hole is no longer needed at the top of the furnace to provide the pass way for the hanging wire. Thus, less thermal disturbance is expected. As a result, the modified Bridgman system can provide a more stable crystal growth environment leading to better crystal qualities.

As discussed previously, temperature gradient and growth rate are two critical parameters for crystal growth by vertical Bridgman technique. The best way to start the crystal growth is to assess the relationship between the growth rate and temperature gradient at solid-liquid interface established in equation (3-1). However, it is difficult to do that in the case of BiI₃ due to the unavailability of its thermal conductivity values. This is probably because BiI₃ will dissociate to Bi and I₂ at 250°C – 300°C,⁵ and I₂ is
very corrosive with extremely high reactivity to metals, which could destroy the instrument for the thermal conductivity measurement. Therefore, in this study, different growth rates and temperature gradients for growing crystals with 0.75 inch diameter were investigated on an educated initial guess basis. Previous studies reported that BiI₃ single crystals have been grown at the conditions of 1 mm/h growth rate with 15°C/cm temperature gradient¹¹ and 1 mm/h growth rate with 5.7°C/cm temperature gradient.¹² As equation (3-4) indicates that the temperature gradient depends on the thermal properties of the furnace, BiI₃ single crystal grown in different furnaces could have very different temperature gradient. The highest temperature gradient allowed in the EDG 24-zone furnace is around 18°C/cm. The temperature variation in each zone is controlled within ±0.5°C, which corresponds to a gradient variation of ±0.2°C/cm. The investigated temperature gradients were then selected as 5, 10, and 15°C/cm to make a distinct difference between them. For each temperature gradient, the crystal growth has been conducted at a speed of 0.5, 1, and 2 mm/h.

3.3.2 Physical Vapor Transport Growth

For the PVT crystal growth, the Pyrex glass ampoule was cleaned using the same procedure described for the MVB growth. A charge of 5 g BiI₃ powder was loaded into a cleaned ampoule with diameter of 0.75 inches. The work charge was first vacuumed to around 4 x 10⁻⁵ mbar and cleaned with ultra high purity grade Ar gas three times, then finally sealed with ultra high purity grade Ar at 700 mbar. Following the crystal growth conditions used by Cuña et al.,⁹ the ampoule end with BiI₃ powder was placed at 310°C and the other end was placed at room temperature. The growth time was 7 days for 5 g of powder. After the growth, the furnace was cooled down at a rate of 1°C/min.
3.3.3 Characterization

A polycrystalline ingot was obtained after the crystal growth by the MVB method. Single crystal samples were cut from the ingot along the cleavage plane (001) with various cross sectional areas and thicknesses. For crystal grown by the PVT method, single crystal platelets with various dimensions were carefully collected. Single crystal samples obtained from both methods were characterized by the following techniques.

3.3.3.1 X-ray Diffraction

X-ray diffraction using CuKα radiation (Philips APD 3720) was used to determine the crystallinity and phase purity of BiI₃ single crystals. The power of the X-ray generator was set to 40 kV and 20 mA. The 2θ angle was scanned from 10° to 60° with a step size of 0.02°.

3.3.3.2 Vickers Hardness

The Vickers hardness of the grown single crystals was measured by a microhardness tester (Buehler MicroMet II). Each sample was measured for 5 indentations and the applying force was 50 g.

3.3.3.3 Etch Pit Density

The dislocation density of the crystal surface was examined by EPD measurement using a KI solution as the etchant. To determine the ideal etchant concentration for EPD measurement, single crystal samples were etched in 5%, 10%, 15%, and 20% weight percent of KI solution respectively, and the etching time varied from 10 sec to 150 sec. After etching, the sample was rinsed with acetone and dried at 120°C for 10 min. The etched sample was weighed to determine the weight loss per unit surface area. The time dependence of the weight loss was calculated for each etchant concentration. The ideal etchant concentration was determined at which the etchant
can effectively remove the mass of BiI₃ single crystal. After that, BiI₃ single crystals grown by the MVB and PVT methods were etched for a specific time. The density of pits was examined by an optical microscope (Nikon Eclipse LV100). For each sample, five randomly selected areas were studied to count the EPD.

### 3.3.3.4 X-ray Rocking Curve

The quality of the grown crystals was inspected by X-ray rocking curve on a Philips analytical MRD X’Pert System, as shown in Figure 3-3.

![X’Pert system for X-ray rocking curve measurement.](image)

The presence of defects such as dislocations and small angle grain boundaries will cause local variation of lattice spacing or plane orientation. For X-ray diffraction in the vicinity of a defect, Bragg’s law cannot be simultaneously satisfied by the perfect lattice and the distorted one, which causes the broadening of X-ray diffraction peak. By performing X-ray rocking curve analysis, the peak broadening of a specific lattice plane can be measured by scanning the incident angle \( \omega \) at a fixed receiving angle \( 2\theta \), as illustrated in Figure 3-4. The full width at half maximum (FWHM) of this peak is generally used to evaluate the quality of a single crystal.\(^{146-148}\) The rocking curve \( \omega \)-scan was conducted at a rate of 0.002°/s with a step size of 0.001°. Each sample was
scanned twice by rotating the sample 90° (φ angle in Figure 3-4) relative to the previous scan, as illustrated in Figure 3-5.

![Figure 3-4. Illustration of rocking curve ω-scan.](image)

Figure 3-4. Illustration of rocking curve ω-scan.

![Figure 3-5. Illustration of the sampling for rocking curve ω-scan. The shadowed bands numbered 1 and 2 represent the X-ray incident area for each scan.](image)

Figure 3-5. Illustration of the sampling for rocking curve ω-scan. The shadowed bands numbered 1 and 2 represent the X-ray incident area for each scan.

### 3.3.3.5 Scanning Electron Microscopy (SEM)

The surface microstructure of the as grown BiI₃ single crystals was characterized using SEM (JEOL 6335F). The freshly cleaved surface was sputtered with carbon film with thickness of around 20 nm. The SEM was operated with an accelerating voltage of 15 kV, a probe current of 10 μA, and a working distance of approximately 15 mm.

### 3.3.3.6 Atomic Force Microscopy (AFM)

To study the surface morphology of the metal contacts, the sample surfaces were examined by AFM (Asylum Research AFM). The AFM tip from Veeco has a triangular
cantilever and a nominal tip radius of 20 nm. The normal stiffness of the tip cantilever is 0.58 N/m. The topography images were acquired in contact mode at a fixed applied load of several nano Newton.

3.3.3.7 X-ray Photoelectron Spectroscopy (XPS)

The stoichiometry of the grown BiI$_3$ single crystal is determined by XPS spectrometer using an Omicron XPS system. The XPS spectra were collected from a freshly cleaved BiI$_3$ crystal surface with an Al Kα monochromatic X-ray (1486.7 eV). The spectra were recorded at a sampling area of 1.3 mm$^2$ and a take-off angle of 55° with pass energy of 22 eV (step size 0.05 eV, integration time 1 sec). The chamber pressure was kept below 5 x 10$^{-10}$ mbar during measurement. The instrument resolution was around 0.1 eV. The peak energies were calibrated using a Ag 3d5/2 peak at 368 eV. The composition of bismuth and iodine was estimated by comparing the photoelectron peak intensities of the Bi 4f with the I 3d core level peaks.

3.3.3.8 X-ray Fluorescence Spectroscopy (XRF)

The stoichiometry of the grown single crystal was also determined by XRF using an Orbis Micro-XRF spectrometer (EDAX Inc.). The XRF spectrometer was operated using a Rh tube at 30 kV. The spot size of the X-ray was 30 μm. The composition of bismuth and iodine was estimated by comparing the X-ray intensities of the Bi M-line with the I L-line in the measured spectrum.

3.4 Results and Discussion

3.4.1 MVB Crystal Growth

3.4.1.1 Determination of Temperature Profile

The concept of vertical Bridgman growth is quite simple. The powder is first heated to the melting temperature and soaked for a period of time. Then the crystal
growth is conducted under certain temperature gradient and moving rate. Finally the entire growth system is cooled back to room temperature. While the temperature gradient and growth rate are vital for producing high quality single crystals, the heat up and cool down cycles are also important for a successful growth run.

As the furnace thermocouples are located at the furnace wall while the growth ampoule is in the center, the temperature difference is presented between the zone temperature reading and the actual temperature of the ampoule. To determine this difference, the central temperature was recorded by a K-type thermocouple placed along the central axis of the furnace. It was observed that the central temperature was around 20°C higher than the temperature reading at the furnace wall. To ensure the complete melting of BiI₃, the highest temperature for the soaking period was set as 440°C. This is based on the fact that ideally BiI₃ will melt at 408°C and the actual soaking temperature will be around 460°C.

The heating rate is not a major concern for BiI₃ as the processing temperature is in the medium range and Pyrex ampoule has a very low thermal expansion coefficient (3.2 x 10⁻⁶/°C). The only concern is to make sure that the furnace temperature does not go up too fast or too slow, as both conditions require additional time to reach thermal equilibrium. Experimentally, the heating rate has been tested at 1, 3, and 5°C/min. It was found that at 3 and 5°C/min heating rates the furnace temperature could not follow the set temperature. The temperature lags were of around 10 and 30°C for the heating rate of 3 and 5°C/min respectively. When the heating rate was lowered to 1°C/min, the furnace temperature completely followed the set point with ±1°C variations. Based on the test result, the heating rate was set at 1°C/min for all the crystal growth runs.
After the furnace reached the maximum temperature, the powder in the growth ampoule may still be lower than this point since heat transfer takes time. A soak period has to be set up to allow every component inside the furnace reach the thermal equilibrium. A K-type thermal couple was attached at the outer wall of the ampoule to test the equilibrium time. It was observed that the temperature was stabilized in the first 30 minutes after reaching the maximum temperature. However, the BiI$_3$ melt inside the ampoule may need longer time to reach thermal equilibrium. A soaking time of 12 hours will be safe enough to thermally stabilize the whole growth system.

After soaking, the furnace was cooled down to 410$^\circ$C at a rate of 1$^\circ$C/min. The corresponding central temperature was around 430$^\circ$C. This is to make sure the overall furnace temperature is still above the melting point of BiI$_3$. Starting from this point, the crystal began to grow at a specific growth rate and temperature gradient described in section 3.3.1. The temperature at which the crystal growth ends is another important parameter needed to be determined. If the crystal growth ends at a high temperature, lattice disorder may happen due to the fast cooling of the atoms with high kinetic energies. On the other hand, ending the crystal growth at a very low temperature is time wasting. It is noted that the crystal growth of BiI$_3$ by PVT method happens at $\sim$250$^\circ$C,\textsuperscript{130} which implies that atoms at this temperature barely have enough kinetic energies to move around. Therefore, in this study, the crystal growth was set to end at 200$^\circ$C, which corresponding to a furnace temperature of 180$^\circ$C. The crystal after growth was cooled to room temperature at a rate of 1$^\circ$C/min. A temperature profile was created based on the above discussion, as illustrated in Figure 3-6. The total growth
time varies with the temperature gradient and growth rate. For example, the growth time for a crystal grown at 10°C/cm and 0.5 mm/h is around 20 days.

![Graph showing temperature versus time](image)

Figure 3-6. Growth recipe of the crystal growth at 10°C/cm and 0.5 mm/h.

### 3.4.1.2 Crystal Growth Result

For crystal growth in 0.75 inch diameter ampoules, it was determined that only three different combinations of growth rates and temperature gradients produced large single crystals: 10°C/cm and 0.5 mm/h; 10°C/cm and 1 mm/h; and 15°C/cm and 0.5 mm/h (Table 3-1). The typical polycrystalline rods and cleavage planes of crystals obtained at different growth conditions are shown in Figure 3-7.

**Table 3-1. Growth conditions for BiI₃ single crystals in 0.75” diameter ampoules.**

<table>
<thead>
<tr>
<th>Temperature Gradient (°C/cm)</th>
<th>Growth Rate (mm/h)</th>
<th>5</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°C/cm</td>
<td>0.5</td>
<td>Polycrystalline</td>
<td>Single crystal</td>
<td>Single crystal</td>
</tr>
<tr>
<td>10°C/cm</td>
<td>1</td>
<td>Polycrystalline</td>
<td>Single crystal</td>
<td>Polycrystalline</td>
</tr>
<tr>
<td>15°C/cm</td>
<td>2</td>
<td>Polycrystalline</td>
<td>Polycrystalline</td>
<td>Polycrystalline</td>
</tr>
</tbody>
</table>

It is noticed that single crystals were obtained at the same temperature gradient (10°C/cm) but different growth rates (0.5 and 1 mm/h) or the same growth rate (0.5 mm/h) but different temperature gradients (10 and 15°C/cm). It is therefore clear that equation (3-1) cannot explain these experimental results. However, one has to keep in
mind that equation (3-1) is established on the steady state condition. A real crystal
growth always happens at a non-steady state, although it may be very close to a steady
state. Therefore, the requirement for crystal growth becomes

\[ K_sG_s - K_LG_L > \rho_sLR \]  \hspace{1cm} (3-27)

which suggests as long as the overall heat flux flowing away from the growth interface
exceeds the rate of latent heat evolution, the growth of single crystal could happen.\textsuperscript{124}

This explains why BiI\textsubscript{3} single crystals were obtained at the three conditions listed in
Table 3-1.

Figure 3-7. Single crystals produced by MVB method, (a) as grown polycrystalline rod;
(b) crystal grown at 10\textdegree C/cm, 0.5 mm/h; (c) crystal grown at 10\textdegree C/cm, 1
mm/h; (d) crystal grown at 15\textdegree C/cm, 0.5 mm/h; (e) crystal grown at 15\textdegree C/cm,
1 mm/h; (f) polycrystalline cross section obtained at rest conditions.

Based on the above discussion, single crystal should also be grown at 15\textdegree C/cm
and 1 mm/h given that single crystal was obtained at 10\textdegree C/cm and 1 mm/h. Actually the
solidification at this condition was characterized by parallel growth of multiple crystals, which had a non-smooth growth interface, as shown in Figure 3-7e. A possible reason for this kind of interface morphology was the thermal fluctuations at the growth interface, a phenomenon that has been commonly observed for other single crystal growths. The growth furnace was observed to have a temperature fluctuation of around ±1°C at a temperature gradient of 15°C/cm, compared to ±0.5°C at a temperature gradient of 10°C/cm. A higher growth rate would cause more fluctuations and non-smooth interface compared to a lower growth rate. Therefore, crystal grown at 15°C/cm and 1 mm/h was under a condition with high thermal fluctuations, which caused the formation of a non-smooth interface. By decreasing the temperature gradient to 10°C/cm or the growth rate to 0.5 mm/h, the thermal fluctuations were suppressed and smooth growth face was obtained. Based on the experimental results, the critical conditions to grow BiI₃ single crystals with a diameter of 0.75 inch can be concluded as a temperature gradient between 10°C/cm and 15°C/cm, and a growth rate between 0.5 mm/h and 1 mm/h. A single crystal with a dimension of 18 x 13 x 5 mm³ has been successfully grown at the temperature gradient of 10°C/cm and growth rate of 0.5 mm/h, as shown in Figure 3-8.

Figure 3-8. BiI₃ single crystal with dimension of 18 x 13 x 5 mm³, the largest crystal size ever reported.
This is the largest crystal size ever reported for BiI3. The previously reported largest BiI3 single crystal was prepared by Nason and Keller with a dimension of 12 x 12 x 4 mm³.\(^{10}\)

### 3.4.2 PVT Crystal Growth

The growth ampoule and a single crystal platelet obtained after PVT growth are shown in Figure 3-9. Many tiny crystals, needles, and platelets were found to stack up together in the ampoule where the temperature was measured to be around 230°C, which was determined to be the growth temperature of the single crystal platelets. The platelets were carefully separated from the polycrystalline mixture by using tweezers and a razor blade. The typical platelet has a surface area of 5 - 20 mm² and a thickness of 100 - 200 μm.

![Figure 3-9. BiI3 single crystals grown by the PVT method.](image)

### 3.4.3 Crystal Structure and Phase Purity

X-ray diffraction was used to determine the crystal structure and phase purity of single crystals grown by the two techniques described before. All the diffraction patterns were almost identical and a typical XRD pattern is shown in Figure 3-10. Only 003, 006, 009, and 0012 reflections parallel to the (001) plane were observed, and the peak positions matched well with the published BiI3 powder diffraction data for a rhombohedral crystal structure (JCPDS PDF# 48-1795).\(^{10}\)
The lattice parameters of the single crystal grown by the MVB method were determined by performing 2θ scans on several selected planes. The scan was conducted by rotating and tilting the single crystal to satisfy the Bragg's condition for a specific plane that is not parallel to the crystal surface. The planes and their corresponding 2θ angle are listed in Table 3-2. The lattice parameters were calculated by least squares fit with values of $a = 7.516 \pm 0.002$ Å and $c = 20.697 \pm 0.003$ Å, which matched well with the published powder diffraction data of $a = 7.519$ Å and $c = 20.721$ Å. The XRD results verified that BiI$_3$ single crystals have been successfully grown by the MVB and PVT methods.

Table 3-2. 2θ angles of selected planes.

<table>
<thead>
<tr>
<th>Planes (hkl)</th>
<th>003</th>
<th>104</th>
<th>107</th>
<th>116</th>
<th>018</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ</td>
<td>12.790</td>
<td>21.920</td>
<td>33.258</td>
<td>35.205</td>
<td>37.371</td>
</tr>
</tbody>
</table>

**3.4.4 Vickers Hardness**

Vickers hardness test is a method to determine the hardness of a material by measuring the size of an indentation produced under force by a pyramid shape diamond.
The angle between the two opposite faces of the pyramid is 136°. After removal of the load, the two diagonals (d1, d2) of the indentation on the surface of the material are measured under a microscope and their average is calculated (Figure 3-11). The area of the sloping surface of the indentation is calculated by

\[ A = \frac{d^2}{2\sin(136°/2)} \approx \frac{d^2}{1.8544} \]  

(3-28)

where d is the mean diagonal of the indentation with a unit of mm. The Vickers hardness (HV number) is then determined by

\[ HV = \frac{F}{A} \approx \frac{1.8544F}{d^2} \]  

(3-29)

where F is the applied force with a unit of Kg.

The Vickers hardness on the (001) surface of single crystals grown by the MVB method was measured and is shown in Table 3-3. Single crystals grown by the PVT method were not subjected to the hardness test as the crystals are too thin. The average HV numbers of the single crystals grown at different conditions showed no significant difference. The results indicated that BiI₃ single crystal is soft with a HV number between 12 and 15. As a comparison, the HV number of a HgI₂ (001) surface is ~22, a 316L stainless steel is 140.

![Figure 3-11. Illustration of Vickers hardness test.](image-url)
Table 3-3. Vickers hardness of (001) surface of BiI₃ single crystals grown by the MVB method.

<table>
<thead>
<tr>
<th>Meas.</th>
<th>d1</th>
<th>d2</th>
<th>HV #</th>
<th>d1</th>
<th>d2</th>
<th>HV #</th>
<th>d1</th>
<th>d2</th>
<th>HV #</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.088</td>
<td>0.089</td>
<td>12</td>
<td>0.082</td>
<td>0.078</td>
<td>14</td>
<td>0.077</td>
<td>0.079</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>0.073</td>
<td>0.088</td>
<td>14</td>
<td>0.093</td>
<td>0.085</td>
<td>12</td>
<td>0.083</td>
<td>0.080</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>0.082</td>
<td>0.089</td>
<td>13</td>
<td>0.088</td>
<td>0.085</td>
<td>12</td>
<td>0.086</td>
<td>0.079</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>0.091</td>
<td>0.088</td>
<td>12</td>
<td>0.082</td>
<td>0.080</td>
<td>14</td>
<td>0.075</td>
<td>0.080</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>0.086</td>
<td>0.087</td>
<td>12</td>
<td>0.082</td>
<td>0.087</td>
<td>13</td>
<td>0.084</td>
<td>0.080</td>
<td>14</td>
</tr>
<tr>
<td>Aver.</td>
<td>13±0.15</td>
<td>13±0.16</td>
<td>14±0.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4.5 Etch Pit Density Measurement

The EPD measurement is generally utilized to determine the quality of semiconductor single crystals. An etching solution is applied on the surface of a crystal and the etching rate increases at dislocation sites resulting in the formation of pits. Therefore, EPD is often used to evaluate the dislocation density of single crystals. In this study, the etchant was KI solution as it was routinely used to reveal dislocations in HgI₂ and PbI₂. The time dependence of the weight loss for different etchant concentrations is shown in Figure 3-12.

![Figure 3-12. BiI₃ etched in different concentration of KI solutions. The unit of weight loss is mg/cm².](image-url)
It was observed that the initial etching rate increased with the etchant concentration. The weight loss reached a maximum after etching approximately 2 minutes for all solutions. The maximum weight loss was around 27 mg/cm$^2$, which corresponded to an etched depth of approximately 50 μm for BiI$_3$. The weight loss curve showed almost no difference once the etchant concentration was higher than 15%. Therefore, 15% KI solution was selected as the etchant for the EPD study.

The optical images of BiI$_3$ single crystal surfaces after etched in 15% KI solution are shown in Figure 3-13. The pits had a curved triangular shape, which represented the atomic arrangement of (001) plane as described in Figure 2-4b. The size of the pits was around 60 μm (the side length of the triangle) after etched for 10 sec. It was observed that the size of the pits increased with the increasing etching time. After etched for 30 sec, the pits started to overlap with each other and the number of pits became uncountable. Therefore the etching time for EPD measurements was determined to be 10 and 20 sec.

The typical images of etch pits for BiI$_3$ single crystals are shown in Figure 3-14. No obvious etched pits were observed for crystals grown by the PVT method even when the etching time was extended from 10 to 60 sec. This indicated that crystals grown by the PVT method had much lower dislocation density than crystals grown by the MVB method.

When counting the number of the pits, if the pit crosses the corner of the area, it is counted as 1/4 pit; if the pit crosses the side, it is counted as 1/2 pit. The pit number was counted in an area of 6.3 x 10$^{-3}$ cm$^2$. The results of EPD measurements are summarized in Table 3-4.
Figure 3-13. Optical images of BiI₃ single crystal surface after etched for time of (a) 10 sec; (b) 20 sec; (c) 30 sec; (d) 40 sec; (e) 50 sec; (f) 60 sec.
Figure 3-14. Etch pits of BiI₃ single crystals grown by MVB and PVT methods. (a) – (c): MVB crystals etched for 10 sec, the crystal was grown at (a) 10°C/cm, 0.5 mm/h; (b) 10°C/cm, 1 mm/h; (c) 15°C/cm, 0.5 mm/h; (d) PVT crystal etched for 10 sec; (e) PVT crystal etched for 60 sec.

It was observed that the number of pits varied from one area to another, which indicated the inhomogeneous distribution of dislocations in the MVB crystal. The EPD didn’t show an apparent increase for a longer etching time (from 10 sec to 20 sec) and the extended time mainly increased the size of the pits, which is more obviously shown in Figure 3-13. The EPD of BiI₃ single crystals grown by the MVB method was on the
order of $10^4$ cm$^{-2}$ and the crystal grown at 10°C/cm and 0.5 mm/h showed the smallest EPD. The EPD value of BiI$_3$ is comparable with other semiconductor crystals such as HgI$_2$ ($\sim 10^3 - 10^5$ cm$^{-2}$) and CZT ($\sim 10^4 - 10^5$ cm$^{-2}$).

Table 3-4. Etch pit density of single crystals grown by the MVB method.

<table>
<thead>
<tr>
<th>Growth condition</th>
<th>Etching time (s)</th>
<th>Number of pits</th>
<th>Average pit #</th>
<th>EPD (10^4 cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Area 1</td>
<td>Area 2</td>
<td>Area 3</td>
<td>Area 4</td>
</tr>
<tr>
<td>10°C/cm 0.5mm/h</td>
<td>10</td>
<td>65.50</td>
<td>60.25</td>
<td>81.50</td>
</tr>
<tr>
<td>10°C/cm 1mm/h</td>
<td>10</td>
<td>87.25</td>
<td>73.50</td>
<td>105.50</td>
</tr>
<tr>
<td>15°C/cm 0.5mm/h</td>
<td>10</td>
<td>91.50</td>
<td>82.50</td>
<td>87.00</td>
</tr>
<tr>
<td>10°C/cm 20</td>
<td>20</td>
<td>83.00</td>
<td>72.50</td>
<td>78.00</td>
</tr>
<tr>
<td>10°C/cm 20</td>
<td>20</td>
<td>82.50</td>
<td>78.00</td>
<td>76.50</td>
</tr>
</tbody>
</table>

3.4.6 X-ray Rocking Curve

X-ray rocking curve characterization is a nondestructive analysis method compared to the EPD measurement. In this study, the X-ray rocking curves of BiI$_3$ (006) plane were measured as this plane showed the highest intensity in X-ray diffraction (Figure 3-10). The X-ray rocking curve $\omega$-scans of BiI$_3$ single crystals grown by MVB and PVT methods were shown in Figure 3-15. Features of extra peaks and shoulders were observed in all the crystals, which suggested that crystal planes in all these samples were not perfectly aligned. Defects such as dislocations and twin planes may account for these features. Multiple small crystals with orientation close to [001] may also exist in these crystals. The plot with log scale can reveal the low intensity features more clearly. The rocking curves scanned at two perpendicular directions for the same sample showed different shape and peak width. This indicated that the distribution of the defects was inhomogeneous in these crystals.

The FWHM of the rocking curves for each sample is summarized in Table 3-5. The crystals grown by MVB method showed similar rocking curve FWHMs thus the
crystal quality could not be differentiated by this technique. On the other hand, the crystal grown by PVT method showed overall smoother peaks and smaller peak width compared to the crystals grown by MVB method. This suggested that crystals grown by PVT method have better quality, which was in agreement with the EPD result.

Table 3-5. FWHM of X-ray rocking curves for BiI₃ single crystals.

<table>
<thead>
<tr>
<th></th>
<th>MVB Crystals</th>
<th>PVT Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10°C/cm and 10°C/cm and 15°C/cm and</td>
<td></td>
</tr>
<tr>
<td>0° scan</td>
<td>0.5 mm/h</td>
<td>0.5 mm/h</td>
</tr>
<tr>
<td>0.1818</td>
<td>0.3438</td>
<td>0.2292</td>
</tr>
<tr>
<td>0.1085</td>
<td>0.1670</td>
<td>0.1839</td>
</tr>
<tr>
<td>90° scan</td>
<td>0.0415</td>
<td>0.1181</td>
</tr>
</tbody>
</table>

Figure 3-15. X-ray rocking curve ω-scans of the single crystals. (a) – (c): single crystals grown by MVB method at a) 10°C/cm and 1 mm/h; b) 10°C/cm and 0.5 mm/h; c) 15°C/cm and 0.5 mm/h; (d) single crystal grown by PVT method. Solid line – linear intensity; circles – log scale intensity.

The rocking curve ω-2θ scan was performed on the MVB and PVT crystals to check the distribution of the (006) d-spacing, as shown in Figure 3-16. It was observed
that the d-spacing distribution for both crystals had wide ranges, which could partially account for the broadening of the rocking curves.

![Rocking curve ω-2θ scan of BiI₃ single crystals indicated the wide distribution of d-spacing.](image)

Figure 3-16. Rocking curve ω-2θ scan of BiI₃ single crystals indicated the wide distribution of d-spacing.

The poor crystalline perfection observed in BiI₃ single crystals was also commonly observed in other iodine compound crystals such as HgI₂ and PbI₂. This was possibly due to the softness of all these materials. Strains induced from the thermal stress during the cooling of the crystal could easily cause the lattice distortion thus the broadening of the rocking curves. For BiI₃ single crystal, similar FWHM values were also reported by Nason and Keller who grew the crystals on a seed using the PVT method. Their rocking curve measurement on (0012) plane showed FWHM values of 600 and 900 sec of arc, corresponding to 0.17° and 0.25° respectively (Figure 3-17).

The rocking curves of BiI₃ have exceedingly large FWHM values compared to other single crystals with similar EPD values. For example, a typical CZT crystal with ~10⁴ cm⁻² EPD value exhibited a rocking curve FWHM of ~0.01°. A high quality GaAs crystal with EPD less than 103 cm-2 showed a rocking curve FWHM of ~0.001°. It should be noted that due to the softness of BiI₃, the crystal could also be deformed.
during cutting and handling, as evidenced in Figure 3-18. It is possible that the peak broadening was exaggerated by these additional strains.

![Figure 3-17. X-ray rocking curves of BiI₃ (0012) planes by Nason and Keller. A and B represent the rocking curves obtained at different sample locations.](image)

![Figure 3-18. Deformation of BiI₃ caused by cutting as in circled area.](image)

### 3.4.7 SEM Characterization

The (001) surface morphologies of BiI₃ single crystal were observed by SEM. The surfaces were clean, smooth, and free of cracks, as shown in Figure 3-19. The deformation caused by cutting was clearly observed at the edge of the single crystal (Figure 3-19a). The layered structure of (001) planes was revealed in Figure 3-19b.
The grey square box observed in Figure 3-19b was the evidence of surface damage caused by the strong electron beams, which illustrated the vulnerability of BiI₃ to electrons.

3.4.8 AFM Characterization

The topographic morphologies of the cleaved BiI₃ surface were characterized by AFM. The surface was observed to be atomically rough with an average surface roughness of 0.484 nm (Figure 3-20).
The atomic layers were revealed in the topographic images with irregular edges, which was possibly due to the weak van der waal’s forces between the layers along [001] direction.

### 3.4.9 XPS Characterization

The elemental composition near the surface of BiI$_3$ single crystal was characterized by XPS. The full scanned XPS spectra are shown in Figure 3-21.

![Figure 3-21. XPS spectrum of freshly cleaved BiI$_3$ single crystal.](image)

On the freshly cleaved surface (1 day exposure in air), only carbon contamination was observed. For the surface with two weeks exposure in atmosphere, O 1s peak was clearly identified. The result suggested that BiI$_3$ was stable in air for a short time, possibly several days. It will be eventually oxidized after a long time exposure in air. Therefore, BiI$_3$ single crystals were stored in inert gas environment to avoid the oxidization.

The Bi 4f and I 3d spectra of the freshly cleaved surface were collected with higher resolution, as shown in Figure 3-22. The properties of these peaks are listed in Table 3-
6. The I/Bi atomic ratio was calculated by the intensity ratio between the I 3d5/2 peak and the Bi 4f peaks. The calculation indicated an iodine deficiency with I/Bi ratio of 2.78.

![XPS spectra of Bi 4f and I 3d for a freshly cleaved BiI₃ crystal surface.](image)

**Figure 3-22.** XPS spectra of Bi 4f and I 3d for a freshly cleaved BiI₃ crystal surface.

**Table 3-6.** Peak properties of Bi 4f and I 3d for a freshly cleaved BiI₃ crystal surface.

<table>
<thead>
<tr>
<th>Element</th>
<th>Line</th>
<th>Peak (eV)</th>
<th>Area</th>
<th>FWHM</th>
<th>Atomic Sensitivity Factors</th>
<th>Norm Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>4f7/2</td>
<td>159.32</td>
<td>8612</td>
<td>0.93</td>
<td>7.4</td>
<td>1163.7838</td>
</tr>
<tr>
<td></td>
<td>4f5/2</td>
<td>164.64</td>
<td>6932</td>
<td>0.94</td>
<td>7.4</td>
<td>936.7568</td>
</tr>
<tr>
<td>I</td>
<td>3d5/2</td>
<td>619.47</td>
<td>35037</td>
<td>1.14</td>
<td>6</td>
<td>5839.3333</td>
</tr>
</tbody>
</table>

**3.4.10 XRF Characterization**

The XRF spectrum of BiI₃ is shown in Figure 3-23. Quantitative analysis was performed by comparing the intensities of Bi M-line to I L-line, as summarized in Table 3-7. The result indicated an I/Bi ratio of 2.54. Considering XRF is not a very sensitive analytical method, an uncertainty of ~10% is generally expected for the quantitative analysis.¹⁶⁴-¹⁶⁵ The stoichiometry determined by XRF was consistent with the XPS characterization. Since XRF has a much higher sampling depth than XPS, the iodine deficiency is considered as the bulk defect of the single crystal.
The stoichiometric deviation of BiI₃ single crystal was also observed by Matsumoto et al. who reported an I/Bi ratio of ~2.9 using XRF analysis. The iodine deficiency issue has been commonly observed in other iodide semiconductor compound such as HgI₂ and PbI₂. It was also reported that BiI₃ tended toward dissociation into Bi and I₂ at 250 – 300°C, which implied that this stoichiometric deviation may come from the evaporation of iodine after the crystal growth.

Table 3-7. Quantitative results of XRF spectrum of BiI₃ single crystal.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si K</td>
<td>35.29</td>
<td>1.15</td>
</tr>
<tr>
<td>Bi M</td>
<td>10297.84</td>
<td>27.96</td>
</tr>
<tr>
<td>I L</td>
<td>11465.62</td>
<td>70.89</td>
</tr>
</tbody>
</table>

3.5 Summary and Conclusions

BiI₃ single crystals have been successfully grown by the MVB and PVT methods. The phase purity of the grown single crystals was verified by XRD. The largest BiI₃ single crystal was obtained with a dimension of 18 x 13 x 5 mm³. Similar to other iodide semiconductor compound, BiI₃ single crystals are soft with measured Vickers hardness between 12 and 15.
Single crystals grown by the MVB method showed high EPD values of $\sim 10^4$ cm$^{-2}$. While the single crystals grown by the PVT method did not show apparent etch pits in 15% KI solution. This suggested that crystals grown by PVT method had much lower dislocation densities, which was verified by X-ray rocking curve characterizations. The rocking curve $\omega$-scans for BiI$_3$ single crystals grown by MVB method showed similar characteristics. Poor crystalline perfection was evidenced by the multiple rocking curve peaks and shoulders. Since MVB is a confined growth method and BiI$_3$ is soft, the poor crystalline perfection was mainly attributed to the residual strains induced during the cooling of the crystal. The deformation during handling and cutting was also accounted for the broad rocking curves.

The surface of BiI$_3$ single crystal was observed to be crack-free and macroscopically smooth by SEM. AFM revealed an atomically rough surface with average roughness of 0.486 nm. XPS spectra revealed that BiI$_3$ will be oxidized if exposed in air over two weeks. The stoichiometry of the grown single crystals was determined to be iodine deficiency by XPS and XRF. The deficiency of iodine was also observed in HgI$_2$ and PbI$_2$, which was attributed to the evaporation of iodine.

Among the crystals grown by the MVB method, those grown at a 0.5 mm/hour growth velocity and 10°C/cm temperature gradient showed the smallest EPD values and fair rocking curve FWHM. Thus, single crystals grown at this condition were selected for the further evaluations.

It has been observed that single crystals grown by MVB method exhibited various flaws and defects, potential avenues to overcome these limitations will be addressed in the future work.
4.1 Introduction

BiI₃ has been reported with different band gap characteristics and values. The experimentally and computationally determined band gap value of BiI₃ was ranging from 1.59 eV to 2.2 eV as summarized in Table 4-1. For instance, Vashchenko and Timofeev measured the absorption spectra of BiI₃ at room temperature and reported an indirect band gap of 1.730 ± 0.005 eV.¹⁰²,¹⁶⁸ Jellison et al. used two-modulator generalized ellipsometry to determine ordinary and extraordinary band gaps of 1.991 ± 0.005 eV and 1.997 ± 0.002 eV at room temperature.¹⁶⁹ Density functional theory (DFT) calculations by Schlüter et al. yielded a direct band gap of ~2.2 eV.¹⁷⁰ However, more DFT calculations by Yorikawa and Muramatsu suggested that BiI₃ has an indirect band gap of approximately 1.59 eV with a rhombohedral crystal structure.¹⁷¹ The much smaller band gap value was ascribed to the well-known, endemic underestimation of band gaps by local density approximation (LDA) calculations. There thus appears to be a discrepancy in the electronic structure and band gap values reported for BiI₃ in the literature. This chapter explores the band gap characteristic of BiI₃ through optical UV-Vis spectra. The possible extrinsic factors (temperature and impurities) that could affect the band gap were discussed. The impurity concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results were compared and discussed with the previously reported band gap characterizations.
4.2 Experimental Procedures

4.2.1 UV-Vis Spectra

In this study, the band gap at room temperature was characterized by measuring optical transmission and reflection spectra at the wavelength of 300 to 800 nm. The sample is a freshly cleaved single crystal with thickness of 0.9 mm. The light source was a Newport ARC lamp housing 66902. A parallel single wavelength light beam was generated through a CornerstoneTM 260, Newport monochromator and incident on the crystal surface at an angle of 3° to the crystal optic axis. The intensity of the incident, reflected and transmitted light was measured separately by a UV-silicon detector (Newport).

The temperature dependence of the band gap was determined by optical transmission spectra from 298 to 330 K using a Varian 50 Bio UV-Vis
spectrophotometer. The crystal was attached to the flat surface of a quartz vial which was imbedded in an aluminum block. Holes were drilled through the top and bottom half of the aluminum block which was connected to a water bath (NESLAB RTE-140). The aluminum block was heated up by the hot water running through the holes. As a result, the quartz vial and the crystal were heated by the surrounding hot aluminum. The temperature of the sample was measured by a k-type thermocouple attached to the sample surface. To effectively absorb the heat, the crystal was cut to 5 x 5 mm$^2$ with 0.1 mm thickness.

4.2.2 Inductively Coupled Plasma - Atomic Emission Spectroscopy

The impurity levels of the crystals were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-Elmer Plasma 3200). The analysis was conducted on an as grown crystal ingot to determine the distribution of the impurity elements. The polycrystalline ingot was cut into segments every 5 mm starting from the tip, as illustrated in Figure 4-1. A small amount of BiI$_3$ crystal (tens of mg) was taken from the central portion of each segment and dissolved in 10% trace-metal grade hydrochloric acid (HCl) to form a 10 mg/mL solution. The elemental impurities analyzed in this study were Cu, Ag, Pb, Ni, Fe, and Si, which are the same impurity elements (except for Si) reported by the vendor. Although Si is not reported to be an impurity element in BiI$_3$ powder, it is important to determine the Si concentration in the crystal to check if there is any contamination coming from the Pyrex glass ampoule. To make a comparison, single crystals were also grown in a quartz ampoule as quartz is generally accepted as a non-contamination container for crystal growth. The impurity concentration in the crystal grown in quartz was measured and compared to those in crystals grown in the Pyrex glass.
4.3 Results

4.3.1 Band Gap Determined by Optical Spectra at Room Temperature

The UV-Vis transmission and reflection spectra were measured from 300 nm to 800 nm at room temperature, and are shown in Figure 4-2. The absorption coefficient $\alpha$ was determined from the experimental spectra by solving the following equation:\(^{174}\)

$$T = \frac{(1-R)^2 e^{-ad}}{1-R^2 e^{-2ad}}$$

(4-30)

where $T$ is transmittance, $R$ is reflectance, and $d$ is the sample thickness. The relation between the absorption coefficient $\alpha$ and incident photon energy ($hv$) can be written as:\(^{175}\)

$$(ahv)^{1/n} = A(hv - E_g)$$

(4-31)

where $\alpha$ is the optical absorption coefficient, $h$ is Planck’s constant, $v$ is frequency of the incident photon, and $E_g$ is the optical band gap. The exponent $n$ depends on the type of optical transition. For direct transition, $n = 1/2$; for indirect transition, $n = 2$. In order to determine the nature of the band gap, both direct and indirect band gap relations were examined.
According to Equation (4-2), by plotting \((\alpha \text{hv})^2\) or \((\alpha \text{hv})^{1/2}\) versus \text{hv} and extrapolating the linear part to \((\alpha \text{hv})^2 = 0\) or \((\alpha \text{hv})^{1/2} = 0\), the optical band gap was determined, as shown in Figure 4-3.

A stepped structure was observed in the \((\alpha \text{hv})^{1/2}\) versus \text{hv} plot, indicating an indirect band characteristic of BiI\(_3\). The band gap value was determined by the average of the two interceptions at \((\alpha \text{hv})^{1/2} = 0\), which gave an indirect band gap of 1.68 ± 0.09 eV.
eV at room temperature. This value is in agreement with experimental value reported in references 7, 106, 166 and 171, but smaller than the values reported in references 104 and 167, as listed in Table 4-1.

4.3.2 Effect of Temperature on Band Gap

The effect of temperature on the band gap was determined by measuring UV-Vis transmission spectra from 298 to 330 K; the results are shown in Figure 4-4. It was observed that the absorption edge shifts to the lower energy side when the temperature is increased. The absorption coefficient $\alpha$ was calculated assuming that the energy loss of the transmitted light was solely due to the sample absorption,

$$\alpha = \frac{1}{d} \ln(T)$$  \hspace{1cm} (4-32)

where $d$ is the sample thickness and $T$ is transmittance. The dependence of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ on the photon energy is plotted in Figure 4-5.

![Figure 4-4. UV-Vis transmission spectra of BiI$_3$ single crystal at different temperatures.](image)

Continuous curves instead of stepped characteristics are observed in the $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot, which indicate that the gap is not indirect band. However, it is important to note that compared with the optical spectra discussed in section 4.3.1, here the
reflectance was not taken into account for the calculation of absorption coefficient. This is particularly relevant because equation (4-3) is only valid for a sample with negligible reflectivity, which is not the case here given the mirror surface of the BiI₃ single crystals investigated here. Therefore, this simplified solution of absorption coefficient will not truly represent the band gap characteristics of BiI₃ as key features may be lost in the $(\alpha hv)^{1/2}$ versus $hv$ plot when $\alpha$ approaches zero.

![Graph](image)

Figure 4-5. a) Dependence of $(\alpha hv)^{1/2}$ on the photon energy; b) dependence of $(\alpha hv)^2$ on the photon energy.
Nevertheless, it is clearly observed that in the UV-Vis transmission spectra the absorption edge of BiI$_3$ red-shifts with increasing temperature (Figure 4-4). The temperature coefficient between 298 and 330 K was calculated based on the plot in Figure 4-5a and the value is about -1.18 x 10$^{-3}$ eV/K. This temperature effect has also been reported by other researchers, as indicated in Table 4-1. This red-shifting of the band gap with temperature has been generally found in many semiconductor materials.$^{176-178}$ An empirical fit has been experimentally determined to describe the band gap as a function of temperature.$^{179}$

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}$$

(4-33)

where $E_g(0)$ is the band gap at absolute temperature, $\alpha$ and $\beta$ are the fitting parameters. Fitting the data obtained from Figure 4-5a gives $E_g(0) = 2.06$ eV, $\alpha = 1.36 \times 10^{-3}$ eV/K and $\beta = 52$ K. The band gap at absolute 0 K is then determined to be 2.06 eV, which is about 0.2 eV smaller than the theoretical value. If $\alpha T/(T+\beta)$ is taken as temperature coefficient of the band gap, this coefficient increases with increasing temperature. Different temperature coefficients with close values have been reported for BiI$_3$. For example, Komatsu and Kaifu obtained temperature coefficient of $-1.8 \times 10^{-4}$ eV/K between 6 and 77 K, and $-3.4 \times 10^{-4}$ eV/K between 77 and 286 K. Vashchenko and Timofeev reported a coefficient of $-9.2 \times 10^{-4}$ eV/K between 85 and 293 K. As a comparison, temperature coefficients of BiI$_3$ were calculated using above fitted parameters and listed in Table 4-2.

It is shown that temperature coefficients obtained in this study have slightly higher values, yet the range of the values have good agreement with those reported in literature.
Table 4-2. Temperature coefficient of BiI₃ calculated based on the fitting parameters.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>6</th>
<th>77</th>
<th>85</th>
<th>286</th>
<th>293</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature Coefficient (eV/K)</td>
<td>-1.4 x 10⁻⁴</td>
<td>-8.1 x 10⁻⁴</td>
<td>-8.4 x 10⁻⁴</td>
<td>-1.2 x 10⁻³</td>
<td>-1.2 x 10⁻³</td>
</tr>
</tbody>
</table>

4.3.3 Effects of Impurities on Band Gap

Band gap narrowing is an effect commonly observed in heavily doped semiconductor materials.¹⁸⁰-¹⁸² The physical mechanisms for band gap narrowing fall into two categories: dopant atoms interacting with the semiconductor and modifying its band structure, and strain introduced by the doping process.¹⁸³ The band gap narrowing effect has a general form of \( \Delta E_g \approx AN^{1/3} \), where \( A \) is constant, and \( N \) is the dopant concentration.¹⁸³ For Si, the band gap narrowing is about 0.02 eV with \( 10^{17} \text{ cm}^{-3} \) dopant concentration.¹⁸⁴ If the impurities in BiI₃ single crystal are considered as an extrinsic dopant and the concentration is high, a similar band gap narrowing effect is expected.

The impurity levels of the BiI₃ powder along with the crystals grown in Pyrex glass and quartz ampoules are reported in Table 4-3. The concentration was calculated based on the mole ratio between the impurity element and BiI₃. The concentration of Pb in the powder and crystals was below the detection limits of ICP-AES.

It was observed that the impurity concentrations of the grown crystal maintained the same level as BiI₃ powder. The crystals grown in Pyrex and quartz ampoules had similar impurity concentrations, which suggested that crystal growth in Pyrex glass ampoule was sufficient to maintain the impurity level of the starting material. This is a great processing advantage given the easier ampoule vacuum sealing of Pyrex when compared to quartz.
The sum of the impurity concentrations for all the analytes were around 20 ppm in the crystal. Given that BiI$_3$ has an atomic concentration of $2.37 \times 10^{22}$ cm$^{-3}$, 20 ppm impurity concentration was converted into an atomic concentration of $4.74 \times 10^{17}$ cm$^{-3}$. This was considerably high doping concentration if all the impurity elements were “doped” into the crystal. It was therefore reasonable to expect that the band gap of BiI$_3$ crystal was narrowed by the impurities.

The impurity distribution in the crystal grown in Pyrex glass ampoule was uniform along the axis of the crystal ingot, as shown in Figure 4-6, which suggested that the impurities was hardly segregated during MVB crystal growth.
4.4 Discussion

The band gap measured at room temperature showed close value to most of the literature listed in Table 4-1 except for reference 95 and 158. Regarding to reference 95, one should be noted that the values were actually taken from the peak energy of the fundamental absorption edge, which should be higher than the intrinsic band gap as the value is taken at the maximum absorption coefficient $\alpha$ instead of at $\alpha$ approaching to zero. In other words, the values reported in reference 95 are related to band gap but with higher energy. They are not the true band gap values, but their change with temperature represents the temperature dependence feature of band gap.

The band gap in reference 158 was measured by ellipsometry. A comparison of spectroscopic ellipsometry and transmission and reflection spectroscopy measurements indicates the relative strengths and weaknesses of the two techniques. Spectroscopic ellipsometry has proven to be useful in extracting the material microstructure in the form of surface features, the index of refraction below the band gap, and the critical point features above the direct gap. This technique, however, lacks the sensitivity when the
absorption coefficient is lower than $\alpha \sim 10^4 \text{ cm}^{-1}$. When the absorption coefficient is extracted using transmission and reflection spectroscopy, sensitivity is retained to $\alpha \sim 10^2 \text{ cm}^{-1}$. Transmission and reflection measurements generally lack sensitivity to the material microstructure, which can lead to erroneous assignment of the above-gap critical point transitions. A combination of these two techniques allows for the accurate determination of the material microstructure and of the optical properties across the given spectral range. Figure 4-7 shows the absorption coefficient extracted by a combination of spectroscopic ellipsometry and transmission and reflection measurements. It is clearly apparent that when the band gap characteristics are above $\alpha \sim 10^4 \text{ cm}^{-1}$ either technique is useful for extraction of the direct or indirect gap, but when the characteristics are lower than $\alpha \sim 10^4 \text{ cm}^{-1}$ transmission and reflection measurements should be used. Thus the different band gap values obtained by UV-Vis and ellipsometry can be attributed to the different range of absorption coefficient used for the data fitting, which is determined by the nature of the techniques. In the case of BiI$_3$, UV-Vis is more accurate to determine the band gap as its band characteristics are lower than $\alpha \sim 10^4 \text{ cm}^{-1}$.

The decrease of band gap value due to increasing temperature and high impurity concentration has been observed in BiI$_3$. However, the effects are rather small, such that they cannot match the difference between experimental and theoretical values. Theoretical DFT calculation gave an indirect band gap value of 2.28 eV.$^{185}$ The experimentally determined value was 2.06 eV at zero temperature by fitting the data obtained from 298 to 330 K. The band gap narrowing caused by impurities has been theoretically studied using DFT calculation, which gave a 0.3 eV decrease of band gap.
for Cu impurity with concentration of $\sim 10^{20}$ cm$^{-3}$. The theoretical study also showed that not every impurity element will cause the band gap narrowing of BiI$_3$. For instance, Si was observed to have no effect on the band structure modification. The band gap narrowing in BiI$_3$ should be far less than 0.3 eV, since the impurity concentration in the crystal ($\sim 10^{17}$ cm$^{-3}$) is much smaller than the value used in DFT calculation.

![Absorption Coefficient](image)

Figure 4-8. The absorption coefficient ($\alpha$) extracted by spectroscopic ellipsometry over a spectral range from 1.88 to 5.15 eV and transmission and reflection below 1.8 eV. Spectroscopic ellipsometry is sensitive to $\alpha > 1000$ cm$^{-1}$, while transmission and reflection measurements for a thick, bulk sample are only sensitive to $\alpha < 50$ cm$^{-1}$. As spectroscopic ellipsometry is a reflection-based technique relying on the complex amplitude reflectance ratios, it retains sensitivity to $\alpha$. Transmission, an intensity based technique, fails to provide accurate values when the material thickness is greater than the penetration depth of light in the material, equal to $1/\alpha$ at a given photon energy.
Although the actual value can not be determined in this study, the band gap narrowing effect should be less than 0.05 eV, as observed in other compound semiconductor materials with similar impurity concentration. Another possible source that could cause the decrease of band gap is the strain within the crystal. Strain could be introduced during crystal growth by the formation of defects such as twin planes, stacking faults and incorporation of impurities. The deviation from stoichiometry as evidenced by XPS analysis could also create strains in the lattice. Strain induced band gap narrowing has been reported for various semiconductor materials. For example, the induced strain in heavily phosphorous-doped (7 x 10^{20} cm^{-3}) silicon was reported to cause ~0.05 eV band gap reduction. Germanium grown on silicon substrate with a tensile strain as large as 0.2% was reported to have a band gap reduction of ~0.03 eV. However, even with the combination effects of temperature, impurity, and strain, the band gap value obtained by experiment is still smaller than the theoretical value. Given that there is no other possible sources that could decrease the band gap, it is concluded that DFT calculation over estimated the band gap by ~0.1 eV.

4.5 Conclusions

The band gap of BiI₃ at room temperature was determined to have indirect character with value of 1.68 ± 0.09 eV by UV-Vis transmission and reflection spectra. The band gap was observed to decrease with increasing temperature. An empirical model has been constructed to fit the temperature dependence of band gap. The fitting result indicated a band gap of 2.06 eV at the absolute zero degree, which is around 0.2 eV lower than the theoretically calculated band gap. The different band gap values obtained by UV-Vis and ellipsometry were attributed to the different absorption coefficient α used to extract the band gap. When the band gap characteristics appear
at $\alpha < 10^4$ cm$^{-1}$, which is the case of BiI$_3$, transmission and reflection measurements should be used to determine the band gap. The impurity concentration in BiI$_3$ single crystal has been determined to be $\sim 10^{17}$ cm$^{-3}$ by ICP-AES. Band gap narrowing was likely to happen at such a high impurity concentration. By comparing the band gap value determined by experiments and DFT calculation, it was concluded that theoretical DFT calculation overestimated the band gap values by about 0.1 eV. In conclusion, the controversy in reported band gap values of BiI$_3$ has been resolved. Temperature and impurities have been determined to be the major factors that affect the band gap of BiI$_3$. In addition, the experimentally determined band gap values also depend on how the data was fitted. For example, the ellipsometry tends to overestimate the band gap value of BiI$_3$ as this technique is only sensitive when the absorption coefficients $\alpha$ are higher than 1000 cm$^{-1}$, while the band characteristics of BiI$_3$ appear at $\alpha$ lower than 100 cm$^{-1}$. 
5.1 Introduction

For detector fabrication, a metal electrode has to be deposited on the surface of BiI₃. The proper choice of the electrode materials is extremely important for the success of the detector. Au and Pd have both been used as electrode materials for BiI₃ detectors. However, the properties of the electrical contacts have never been reported. It is important to understand how the metal contact interacts with the substrate. The reactivity of the metal-semiconductor interface should be used as a guide for the selection of contact material. X-ray photoelectron spectroscopy (XPS) has been widely used to explore the metal-semiconductor interfaces with great success at explaining and predicting the reactivity of the interfaces. In this study, different electrode materials of Au, Pd, and Pt have been sputter coated on the surfaces of BiI₃ single crystals. The metal-BiI₃ interface has been studied by XPS and AFM. The resistivity of BiI₃ single crystals with different contact materials have been measured and compared.

5.2 Experiment Procedures

5.2.1 XPS

5.2.1.1 Principles of XPS

XPS is an electron spectroscopic method that uses monoenergetic soft X-rays to eject electrons from the inner shell orbitals of a sample and analyzes the energy of the detected electrons. In this study, the X-ray source is a monoenergetic Al Kα (1486.7 eV) X-ray. The kinetic energy of an ejected electron is given by

\[ E_k = h\nu - E_b - \varphi_s \]  

(5-34)
where \( hv \) is the energy of the photon, \( E_b \) is the electron binding energy which is the energy difference between the Fermi level and the energy of the atomic orbital from which the electron originates, and \( \phi_s \) is the work function of the spectrometer. Since an atom has multiple orbitals, the corresponding photoelectron spectrum has a variety of peaks that are named according to the orbital (\( l = 0, 1, 2, 3 \ldots \) denoted as s, p, d, f \ldots) and spin (\( s = \pm 1/2 \)) quantum numbers. The total momentum of the photoelectrons (\( J = l + s \)) is included in the labeling of a measured photoelectron peak (e.g., Bi 4f7/2 where \( l + s = 3 + 1/2 = 7/2 \)). The electron binding energy of an element varies with different compounds due to the change of electronic environment. Therefore XPS can be used to identify the chemical state of the materials being analyzed. Since the energy of the X-ray source is low, the penetration depth of the photons is on the order of micrometers. Only those electrons that originate within tens of angstroms below the solid surface can escape the surface without appreciable energy loss, which makes XPS majorly used as a surface analytical technique.

5.2.1.2 Sample Preparation for XPS

The (001) surface of BiI\(_3\) single crystal was cleaved in air by peeling off the top layer of the crystal using Scotch tape. The cleaved surface was sputtered with Au, Pd, and Pt metals with thickness of around 1 nm using Kurt J. Lesker CMS-18 multi target sputter system. The sputtering was conducted in a vacuum chamber with a pressure of \( 10^{-8} \) torr at a deposition speed of around 0.5 nm/s at room temperature. A freshly cleaved surface of a BiI\(_3\) single crystal was used as a reference. X-ray photoelectron spectra were collected by an Omicron XPS system with an Al K\( \alpha \) monochromatic X-ray (1486.7 eV). The spectra were recorded at a sampling area of 1.3 mm\(^2\) and a take-off
angle of 55° with pass energy of 22 eV and step size 0.05 eV. The chamber pressure was kept below 5 \times 10^{-10} \text{ mbar} during measurement. The instrument resolution was < 0.1 eV. The peak energies were calibrated using a Ag 3d5/2 peak at 368 eV. The studied elements included bismuth, iodine, gold, palladium, platinum, carbon, and oxygen.

5.2.2 Atomic Force Microscopy (AFM)

To study the surface morphology of the metal contacts, the sample surfaces were examined by AFM with an Asylum MFP-3DTM Research AFM. The AFM tip from Veeco has a triangular cantilever and a nominal tip radius of 20 nm. The normal force constant of the tip cantilever is 0.58 N/m. The topography images were acquired in contact mode at a fixed applied load of several nN.

5.2.3 I-V Characterization

The resistivity of BiI₃ single crystals with different electrodes was studied by I-V characterization using an Agilent 4155B semiconductor parameter analyzer. Samples were prepared by sputtering Au, Pd, and Pt on the freshly cleaved surface resulting in an electrode thickness of ~200 nm. The sputtering was conducted at the same conditions as described for the XPS samples. Pt wires were attached to the electrodes using silver paste (SPI® Supplies) for electrical connection.

5.3 Results and Discussion

5.3.1 The XPS Spectra

The XPS core-level spectra of all the elements detected are shown from Figure 5-1 to 5-3. The observed elemental binding energies are summarized in Table 5-1. The binding energies of each element in different compounds are given in Table 5-2.
Figure 5-1. XPS spectra of Bi 4f and I 3d for the freshly cleaved Bil₃ (001) surface and surface with Au, Pd, and Pt electrodes.

In the following discussion, the sample without deposited metal is called Bil₃ sample, and the samples with deposited metallic contacts are named Au, Pd, and Pt samples respectively. A quick survey of the XPS spectra reveals that the Au sample maintains the chemical environment of Bil₃, while Pd and Pt show interactions with the substrate. The detailed discussion for each sample is given in the following sections.
Figure 5-2. X-ray photoelectron spectra of Au 4f, Pd 3d, and Pt 4f on the surface of BiI₃ single crystals.
Figure 5-3. X-ray photoelectron spectra of C 1s and O 1s for all the samples.

<table>
<thead>
<tr>
<th>Peak</th>
<th>BiI₃ sample</th>
<th>Au sample</th>
<th>Pd sample</th>
<th>Pt sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi 4f7/2</td>
<td>159.2</td>
<td>159.1</td>
<td>158.6</td>
<td>157.1</td>
</tr>
<tr>
<td>I 3d5/2</td>
<td>619.4</td>
<td>619.1</td>
<td>619.3</td>
<td>619.0</td>
</tr>
<tr>
<td>C 1s</td>
<td>284.7</td>
<td>284.6</td>
<td>284.0</td>
<td>284.3</td>
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<tr>
<td>O 1s</td>
<td></td>
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<td>529.9</td>
<td>533.0</td>
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<tr>
<td>Au 4f7/2</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd 3d5/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt 4f7/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.3.1.1 Au Sample

The XPS spectra of the Au sample show peak positions of Bi 4f and I 3d very close to those of the BiI₃ sample; and the Au 4f spectrum exhibits the same peak
positions with that of a pure gold. The results suggest that Bi, I, and Au maintain their respective chemical state and there is no chemical interaction between Au and BiI$_3$. The C 1s and O 1s spectra are shown in Figure 5-4.

Figure 5-4. Deconvolution of XPS spectra for the Au sample peaks (a) C 1s and (b) O 1s.

The C 1s spectrum of the Au sample can be deconvoluted into two peaks with the peak at 284.5 eV assigned to amorphous carbon$^{198}$ and the peak at 285.7 eV assigned to carbon species bound to oxygen$^{199-201}$ (Figure 5-4a). Two distinct peaks are observed in O 1s spectrum (Figure 5-4b). The peak at 532.2 eV is attributed to oxygen atoms bound to carbon.$^{199}$ The peak at 529.9 eV could be assigned to oxygen atoms in Au$_2$O$_3$ (530.2 eV)$^7$ or atomic O adsorbed at Au surface (530.2 eV).$^{199}$ Since there is no indication of any Au-O bond in the Au 4f spectrum, this peak is assigned to atomic O adsorbed at the Au surface.

5.3.1.2 Pd Sample

Peak shifting of Bi 4f and Pd 3d is observed, which indicates the existence of an interfacial reactivity. The iodine peaks remain the same as the BiI$_3$ sample. The deconvolution of Bi 4f, Pd 3d, C 1s, and O 1s spectra are shown in Figure 5-5. The properties of the fitted peaks and their assignments are summarized in Table 5-3.
Figure 5-5. Deconvolution of XPS spectra of the Pd sample for (a) Bi 4f, (b) Pd 3d, (c) C 1s, and (d) O 1s.

In the Bi 4f7/2 region, three peaks are identified at 157.1, 158.5, and 159.2 eV, which are consistent with the literature values assigned to bismuth atoms in metallic bismuth,\textsuperscript{194} Bi\textsubscript{2}O\textsubscript{3},\textsuperscript{195} and BiI\textsubscript{3}\textsuperscript{193} respectively. However, the assignment of Bi\textsubscript{2}O\textsubscript{3} is not plausible as the corresponding amount of oxygen is not observed in the O 1s spectrum. The peak at 158.5 eV is possibly due to bismuth atoms in a reduced iodine environment (BiI\textsubscript{3-x} with x < 3). The Pd 3d5/2 peak deconvolutes into two peaks at 335.0 and 336.5 eV, which are assigned to palladium atoms in metallic palladium\textsuperscript{193} and PdI\textsubscript{2}\textsuperscript{12} respectively.
Table 5-3. Peak properties of Bi 4f, Pd 3d, Pd 3p, C 1s, and O 1s observed in the Pd sample.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Position (eV)</th>
<th>Element</th>
<th>FWHM (eV)</th>
<th>Area</th>
<th>ASF</th>
<th>Corrected Area</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi 4f</td>
<td>157.1</td>
<td>Bi 4f7/2</td>
<td>0.87</td>
<td>716</td>
<td>7.4</td>
<td>97</td>
<td>Bi</td>
</tr>
<tr>
<td>Bi 4f</td>
<td>158.5</td>
<td>Bi 4f7/2</td>
<td>0.87</td>
<td>460</td>
<td>7.4</td>
<td>62</td>
<td>Bi</td>
</tr>
<tr>
<td>Bi 4f</td>
<td>159.2</td>
<td>Bi 4f7/2</td>
<td>0.87</td>
<td>152</td>
<td>7.4</td>
<td>21</td>
<td>BiI3-x</td>
</tr>
<tr>
<td>Bi 4f</td>
<td>162.4</td>
<td>Bi 4f5/2</td>
<td>0.87</td>
<td>537</td>
<td>7.4</td>
<td>73</td>
<td>Bi</td>
</tr>
<tr>
<td>Bi 4f</td>
<td>163.8</td>
<td>Bi 4f5/2</td>
<td>0.87</td>
<td>345</td>
<td>7.4</td>
<td>47</td>
<td>BiI3-x</td>
</tr>
<tr>
<td>Bi 4f</td>
<td>164.4</td>
<td>Bi 4f5/2</td>
<td>0.87</td>
<td>114</td>
<td>7.4</td>
<td>15</td>
<td>BiI3</td>
</tr>
<tr>
<td>Pd 3d</td>
<td>335.0</td>
<td>Pd 3d5/2</td>
<td>1.03</td>
<td>4512</td>
<td>4.6</td>
<td>981</td>
<td>Pd</td>
</tr>
<tr>
<td>Pd 3d</td>
<td>336.5</td>
<td>Pd 3d5/2</td>
<td>1.03</td>
<td>6796</td>
<td>4.6</td>
<td>1477</td>
<td>PdI2</td>
</tr>
<tr>
<td>Pd 3d</td>
<td>340.3</td>
<td>Pd 3d3/2</td>
<td>1.03</td>
<td>2978</td>
<td>4.6</td>
<td>647</td>
<td>Pd</td>
</tr>
<tr>
<td>Pd 3d</td>
<td>341.7</td>
<td>Pd 3d3/2</td>
<td>1.03</td>
<td>4486</td>
<td>4.6</td>
<td>975</td>
<td>PdI2</td>
</tr>
<tr>
<td>C 1s</td>
<td>283.9</td>
<td>C 1s</td>
<td>1.38</td>
<td>871</td>
<td>0.25</td>
<td>3484</td>
<td>amorphous carbon</td>
</tr>
<tr>
<td>C 1s</td>
<td>285.6</td>
<td>C 1s</td>
<td>1.38</td>
<td>143</td>
<td>0.25</td>
<td>572</td>
<td>C bound to O</td>
</tr>
<tr>
<td>O 1s</td>
<td>533.1</td>
<td>Pd 3p3/2</td>
<td>3.69</td>
<td>5862</td>
<td>1.43</td>
<td>4099</td>
<td>Pd</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.1</td>
<td>O 1s</td>
<td>1.80</td>
<td>378</td>
<td>0.66</td>
<td>573</td>
<td>O bound to C</td>
</tr>
</tbody>
</table>

The C spectrum of the Pd sample has two peaks with the one at 283.9 eV assigned to amorphous carbon and the one at 285.6 eV assigned to carbon species bound to oxygen. The O 1s spectrum is dominated by Pd 3p3/2 peak at 533.1 eV. The intensity of this peak (area under the peak) is consistent with the peak intensity in Pd 3d spectrum, which validates this peak assignment. The identification of oxygen peak in O 1s spectrum is difficult as the majority peak intensity is contributed by Pd atoms. The peak is fitted at 532.1 eV with a fixed 1:1 intensity ratio to the corresponding C 1s peak at 285.6 eV in C 1s spectrum.

XPS analysis indicates the existence of metallic Bi and PdI2 at the Pd-BiI3 interface, which suggests that Pd reacts with BiI3. The majority of the bismuth elements on the surface exist in the form of metallic Bi (~54%) and BiI3-x (~35%), with a small portion (~11%) that remains as BiI3. The reactivity between Pd and iodine-rich crystals
has been previously reported. However, Pd is still widely used as the electrode contacts for iodide compound materials such as Hgl₂ and PbI₂. There is no discussion on how this Palladium-iodine reactivity will affect the detector performance. This suggests that a careful re-evaluation of the electrode contacts for these materials is necessary.

5.3.1.3 Pt Sample

Similar to the Pd sample, peak shifting is also observed in the Bi 4f spectrum in the Pt sample. The Pt 4f peaks exhibit an asymmetric feature, indicative of multiple chemical states for the Pt atoms found in the interfacial region. However, this asymmetry is not due to reactivity therefore no attempt is made to deconvolute the peaks. The similar peak feature has been previously observed in Pt nanoparticles on pyrolytic graphite surfaces. Since Pt was reported to have different electronic configurations for surface and bulk atoms, the asymmetric peak was explained due to the surface Pt atoms in the 5d⁶6s¹ configuration, bulk Pt atoms in the 5d⁸6s² configuration, and surface Pt absorbed oxygen. The deconvolution of Bi 4f, I 3d, C 1s, and O 1s spectra of the Pt sample are shown in Figure 5-6. The peak properties and their assignments are summarized in Table 5-4.

The assignment for Bi 4f spectrum is similar to that in Pd sample. The Bi 4f7/2 peaks at 157.1, 158.3, and 158.9 eV are assigned to bismuth atoms in metallic bismuth, Bil₃-x, and Bil₃ respectively. The existence of I₂ is evidenced by the peak at 619.4 eV in I 3d spectrum. The two peaks in C 1s spectrum are assigned to amorphous carbon at 284.0 eV and carbon species bound to oxygen at 285.9 eV. The O 1s spectrum deconvolutes into two peaks with the one at 529.5 eV assigned to oxygen bound to Pt
and the one at 532.0 eV assigned to oxygen bound to carbon. The uphill tail in the low energy side of O 1s spectrum is the trail of Pt 4p3/2 peak at 520 eV.\textsuperscript{193}

Figure 5-6. Deconvolution of XPS spectra of the Pt sample for (a) Bi 4f, (b) I 3d, (c) C 1s, and (d) O 1s.

The XPS results indicate that Pt is not good as the contact material for BiI\textsubscript{3} either. The effect of Pt on the surface of BiI\textsubscript{3} is different from that of Pd. Here the presence of Pt causes the reduction of BiI\textsubscript{3}. But unlike Pd, Pt does not involve in the reaction. The function of Pt in this case is similar to that of a catalyst.
Table 5-4. Peak properties of Bi 4f, I 3d, C 1s, and O 1s observed in the Pt sample.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Position (eV)</th>
<th>Element</th>
<th>FWHM (eV)</th>
<th>Area</th>
<th>ASF</th>
<th>Corrected Area</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi 4f</td>
<td>157.1</td>
<td>Bi 4f7/2</td>
<td>0.86</td>
<td>2303</td>
<td>7.4</td>
<td>311</td>
<td>Bi</td>
</tr>
<tr>
<td>Bi 4f</td>
<td>158.3</td>
<td>Bi 4f7/2</td>
<td>0.86</td>
<td>1501</td>
<td>7.4</td>
<td>203</td>
<td>BiI_{3-x}</td>
</tr>
<tr>
<td>Bi 4f</td>
<td>158.9</td>
<td>Bi 4f7/2</td>
<td>0.86</td>
<td>891</td>
<td>7.4</td>
<td>120</td>
<td>BiI_3</td>
</tr>
<tr>
<td>Bi 4f</td>
<td>162.4</td>
<td>Bi 4f5/2</td>
<td>0.86</td>
<td>1727</td>
<td>7.4</td>
<td>233</td>
<td>Bi</td>
</tr>
<tr>
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<td>163.6</td>
<td>Bi 4f5/2</td>
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<td>1125</td>
<td>7.4</td>
<td>152</td>
<td>BiI_{3-x}</td>
</tr>
<tr>
<td>Bi 4f</td>
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<td>Bi 4f5/2</td>
<td>0.86</td>
<td>669</td>
<td>7.4</td>
<td>90</td>
<td>BiI_3</td>
</tr>
<tr>
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<td>I 3d5/2</td>
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<td>6</td>
<td>1731</td>
<td>BiI_3</td>
</tr>
<tr>
<td>I 3d</td>
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<td>I 3d5/2</td>
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<td>4365</td>
<td>6</td>
<td>728</td>
<td>I_2</td>
</tr>
<tr>
<td>I 3d</td>
<td>630.1</td>
<td>I 3d3/2</td>
<td>1.12</td>
<td>7555</td>
<td>N/A</td>
<td></td>
<td>BiI_3</td>
</tr>
<tr>
<td>I 3d</td>
<td>630.9</td>
<td>I 3d3/2</td>
<td>1.12</td>
<td>2550</td>
<td>N/A</td>
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<td>I_2</td>
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<tr>
<td>C 1s</td>
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<td>C 1s</td>
<td>1.46</td>
<td>884</td>
<td>0.25</td>
<td>3536</td>
<td>amorphous carbon</td>
</tr>
<tr>
<td>C 1s</td>
<td>285.9</td>
<td>C 1s</td>
<td>1.46</td>
<td>259</td>
<td>0.25</td>
<td>1036</td>
<td>C bound to O</td>
</tr>
<tr>
<td>O 1s</td>
<td>529.5</td>
<td>O 1s</td>
<td>1.59</td>
<td>185</td>
<td>0.66</td>
<td>280</td>
<td>O bound to Pt</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.0</td>
<td>O 1s</td>
<td>1.59</td>
<td>624</td>
<td>0.66</td>
<td>945</td>
<td>O bound to C</td>
</tr>
</tbody>
</table>

5.3.2 AFM Analysis

AFM characterization has been used to check the distribution of the sputtered metals on the surface of BiI₃ (Figure 5-7). It is observed that Au fully covers the BiI₃ surface while Pd and Pt form islands, which indicates a completely wetting of Au on the BiI₃ surface while non-wetting characteristic of Pd and Pt. The islands on the Pt sample surface are more sparsely distributed with higher height compared to the Pd sample. To verify if the islands are formed by the deposited metals or by other species produced in the metal-BiI₃ interaction, the volume of the islands is calculated using an image processing software (Scanning Probe Image Processing, SPIPTM) by analyzing the scanned histogram of the surface. The calculated island volume for Pd sample is $4.6 \times 10^6$ nm$^3$ on a 4 μm$^2$ area, which is corresponding to a thickness of 1.15 nm if the Pd island volumes were evenly spread on the surface. This matches well with the
experimentally deposited thickness of 1 nm and suggests that the islands are mainly formed by Pd. The island volume on Pt sample is calculated to be $7.7 \times 10^8$ nm$^3$ on a 100 μm$^2$ area, which is corresponding to a deposited thickness of 7.7 nm. This result has a large deviation from the experiment (1 nm), which suggests that species generated by the reaction, i.e. I$_2$, may deposit on the surface.

Figure 5-7. AFM image and 3D view of topography for the (a) Au sample, (b) Pd sample, and (c) Pt sample.
5.3.3 I-V Characterization

The resistivity of BiI$_3$ single crystals has been measured with Au, Pd, and Pt electrodes. The crystal samples were cut from adjacent positions of a large single crystal to minimize the sample variation. The I-V curves for crystals with different electrodes are shown in Figure 5-8. It is observed that the crystal with Au electrodes has the highest resistivity, and the one with Pd electrodes shows the lowest, as summarized in Table 5-5.

![Figure 5-8. I-V curves for BiI$_3$ single crystals with Au, Pd, and Pt electrodes.](image)

The similar results were also reported by Fornaro et al. on BiI$_3$ crystals grown by PVT method. Given that Bi$^{3+}$ ions are reduced to metallic Bi at the Pd-BiI$_3$ interface, the Bi atoms could drift across the crystal body under an external electric field. This will decrease the effective thickness between the electrodes. Consequently, the measured resistivity is smaller than the actual value.

Based on the XPS results, Au is expected to be physically contacted with BiI$_3$, the measured resistivity thus represents a more accurate value of this material. The
sample with Pt electrodes shows resistivity in between, which is possibly due to the drift of Bi$^{3+}$ ions resulting from less binding of iodine.

Table 5-5. Sample information and resistivity of BiI$_3$ single crystals for I-V characterization.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Electrode</th>
<th>Surface Area (cm$^2$)</th>
<th>Thickness (cm)</th>
<th>Resistivity $10^9$ (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au</td>
<td>0.260</td>
<td>0.075</td>
<td>1.85</td>
</tr>
<tr>
<td>2</td>
<td>Pd</td>
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<td>0.075</td>
<td>0.28</td>
</tr>
<tr>
<td>3</td>
<td>Pt</td>
<td>0.251</td>
<td>0.076</td>
<td>0.61</td>
</tr>
</tbody>
</table>

5.4 Conclusions

XPS characterization indicates that sputtered Pd and Pt have chemical interactions with BiI$_3$, while Au is observed to be unreactive with BiI$_3$. Pd reacts with BiI$_3$ and forms metallic Bi and PdI$_2$. Pt does not react with BiI$_3$ but functions as a catalyst and causes the reduction of Bi$^{3+}$ ions. The I-V characterization collaborates with the XPS result, and the highest resistivity is obtained from sample with Au electrodes. It is concluded that Au should be used as the electrode contact for BiI$_3$, while Pd and Pt are not recommended. Since the reactivity is observed to be between Pd and iodine, and Pd has long been used as electrode material for Hgl$_2$ and PbI$_2$, this suggest that an evaluation of the interface between Pd and these material is necessary for a better understanding of this interface issue.
CHAPTER 6
SUMMARY AND FUTURE WORK

6.1 Summary

The increasing demand for room temperature gamma-ray detectors encourages the discovery and development of high quality compound semiconductor materials. The required material properties include high density and atomic numbers for high gamma-ray detection efficiency; moderate bandgap between 1.5 eV and 3 eV for room temperature operation and generation of large number of electron-hole pairs, and high resistivity for improved signal to noise ratio. BiI₃ meets all these criteria thus has the potential to be a successful material for room temperature gamma-ray detection applications.

Crystal growth is the most challenging and time-consuming stage of developing a new detector material. This work presented the efforts of growing large volume BiI₃ single crystals using MVB method. The whole growth process is composed of different stages including heating up from room temperature to the maximum process temperature, soaking for a period of time, cooling down to growth temperature, crystal growth, and post-growth cooling down to room temperature. Each stage has been carefully designed and tested to ensure the smooth growth run. The crystal growth was conducted at a total of nine growth conditions (variation of growth rate and temperature gradient at solid-liquid interface), among which only three conditions produced single crystals. The phase purity of the grown single crystals was verified by XRD. The quality of the single crystals was characterized by EPD measurement and X-ray rocking curve ω-scans. For EPD measurement, the etching recipe was determined to be 10 sec immersion in 15% KI solution. The observed EPD values for all the crystals were in...
the order of magnitude of $\sim 10^4$ cm$^{-2}$, which was comparable to other compound semiconductor crystals such as HgI$_2$ and lab produced CZT, but one order of magnitude higher than the commercial CZT crystals. The high EPD values indicated the high dislocation densities in the crystals. Among the crystals grown by MVB method, the one grown at 10$^\circ$C/cm and 0.5 mm/h showed the smallest average EPD values. The rocking curve $\omega$-scan peaks for all the crystals showed similar FWHM and peak characteristics. Peak broadening with multiple peaks and shoulders were observed. The poor crystalline perfection was commonly observed among the iodide compound crystals such as HgI$_2$ and PbI$_2$, which implied that the imperfections were possibly caused by the residual strains induced during the cooling of the crystals due to the softness of these materials. In addition, the deformation during handling and cutting could also contribute to the broadening of the rocking curves. Although the BiI$_3$ single crystals grown at three different conditions did not show distinct differences of EPD values and rocking curve characteristics, the crystals grown at 10$^\circ$C/cm and 0.5 mm/h were selected for further studies due to their slightly better qualities. A single crystal with a dimension of 18 x 13 x 5 mm$^3$, the largest crystal size ever reported for BiI$_3$, has been obtained at this growth condition.

The cleaved surface of BiI$_3$ was characterized by SEM and AFM respectively. The SEM characterization indicated a crack-free and macroscopically smooth surface. The AFM topographic image revealed an atomically rough (001) surface with average roughness of 0.486 nm. The irregular edges of the atomic layers were attributed to the weak van der waals forces between the layers. The chemical composition at the surface of BiI$_3$ was characterized to be of BiI$_{2.78}$ by XPS. The iodine deficiency was
attributed to the dissociation of BiI₃ into Bi and I₂ during cooling of the crystal, and the evaporation of iodine when exposed in air. The surface oxidation was also observed for BiI₃ crystals exposed in air for over two weeks, which suggested that a proper sealing or inert gas environment is necessary for the crystal storage.

Through UV-Vis transmission and reflection spectra, the band gap of BiI₃ was characterized to be of 1.68 ± 0.09 eV with indirect transition characteristic. The band gap value of BiI₃ was observed to decrease with increasing temperature, which is commonly observed in semiconductor materials. The impurity concentrations in commercial powder and BiI₃ crystals were observed to be as high as 10^{17} cm⁻³, at which the band gap narrowing effect was likely to happen. The band gap value determined in this work was consistent with previous studies using UV-Vis spectra. The indirect band transition was confirmed by the most recent theoretical calculation on the band structure of BiI₃ using DFT. The large difference between the band gaps determined by UV-Vis spectra and ellipsometry was attributed to the different absorption coefficient α used to extract the band gap. For BiI₃, band gap determined by UV-Vis spectra was more accurate.

The metal-semiconductor interface was characterized for BiI₃ (001) surface by XPS. The results indicated that the commonly used Pd electrode reacted with BiI₃ and produced Bi metal and PdI₂ on the surface. As another commonly used electrode material, Au was unreactive with BiI₃. The third contact material, Pt, was observed to cause the reduction of Bi^{3+} ions, although it did not react with BiI₃. I-V characterization indicated that BiI₃ crystal with Au electrode exhibited the highest resistivity, which more accurately represented the resistivity of BiI₃ since only Au was physically contacted with
the crystal surface. Based on the above analysis, Au was recommended for the contact material for BiI₃, while Pd and Pt should not be used without prior surface modification or passivation steps. The observed reactivity between Pd and BiI₃ could be extended to other iodine based semiconductor materials such as Hgl₂ and PbI₂. This suggested that the re-evaluations of the contact metals for all these materials are necessary.

Through the characterizations on BiI₃ single crystals grown in this work, it was found that the crystals have high impurity concentrations and dislocation densities. The crystal quality is not comparable to the commercial CdTe and CZT crystals. The future work should focus on resolving these problems and developing BiI₃ towards a room temperature gamma-ray spectrometer.

6.2 Future work

6.2.1 Tilted Growth

For vertical Bridgman crystal growth, the effect of gravity force could be significant. The mechanical stress due to the gravity force can be expressed as

\[ \sigma = \rho g V / A \]  

where \( \rho \) is the density of the crystal, \( g \) is the gravitational constant, \( V \) is the volume of the crystal and \( A \) is the cross area at which the stress is measured. For BiI₃, \( \rho = 5.8 \) g/cm³, \( g = 9.81 \) N/kg, the stress can be simplified as

\[ \sigma [Pa] = 569.0 (V / A) [cm] \]  

The ratio \( V/A \) varies with the location on the crystal. Since tipped ampoule was used for the crystal growth, the stress at the tip area could be very large. For example, for the crystal with 1 cm long tip of 3 cm in total length, the stress at the tip area with 1 mm diameter could be as high as 120 kPa (Figure 6-1).
The critical resolved shear stress (CRSS) reported for HgI₂ was around 0.1 MPa on (001) face. Considering BiI₃ is softer than HgI₂, appreciable slip may occur at such a high stress, which could lead to the observed high dislocation density and poor crystal perfection.

The mechanical stress induced by gravity could be alleviated by tilting the ampoule for crystal growth. On one hand, the cross-section area will be increased by the tilting thus decreasing the stress applied on it. On the other hand, partial of the gravity force will be taken by the ampoule therefore the actual gravity force applied on the crystal will be greatly decreased. The angle of tilting needs to be experimentally determined for the crystal growth.

6.2.2 Synthesis of High Purity BiI₃ Powder

The ICP-AES measurement indicated that even the commercial BiI₃ powder have high impurity concentration. One way to solve this problem is to synthesize BiI₃ in lab using high purity (99.999% and up) Bi and I₂ particles. The synthesis could be done by sublimation method in a gas flowing ampoule, as illustrated in Figure 6-2.

In this setup, Argon gas at a flow rate of 40 cc/min is passed over I₂ at 25°C and the gas mixture reacts with Bi at 310°C when passing over it. The produced BiI₃ vapor passes along with the Argon gas and deposits at 210°C for the crystal growth.
excess I$_2$ condenses at the coolest part of the apparatus. The boat that holds bismuth and Bil$_3$ crystals in the illustration is necessary to provide a removable section in the growth region so that the crystals could be easily separated from the condensed iodine. The collected high purity crystal platelets can be used for the MVB crystal growth. Although Pyrex glass ampoule was used in the original study, quartz or fused silica tube was recommended in other studies to largely reduce the possible contaminations. A horizontal tube furnace with precise temperature control is required for this process.

Figure 6-2. Illustration for the sublimation growth of Bil$_3$. (After Curtis and Brunner$^{213}$)

### 6.2.3 Sublimation of Bil$_3$ Powder

Another way to improve the purity of the crystal could be done by multiple sublimation of the commercial powder. The experimental setup can use the same one shown in Figure 6-2. Here the bismuth in Figure 6-2 will be replaced by Bil$_3$ powder. Since Bil$_3$ tends to dissociate to Bi and I$_2$ at 250 – 300°C, keep supplying iodine vapor could help suppress this reaction. One would immediately realize that the crystal platelets produced by the sublimation method could also be further purified by this method, which should be included in the future work.
6.2.4 Post-growth Annealing

High dislocation density was observed in the single crystals grown by MVB method. The dislocation density could be decreased by performing thermal annealing on the grown crystals. This method has been generally used for the post-growth treatment of single crystals to improve the crystal qualities.\textsuperscript{214-217} The dislocation density after annealing has been reported to be reduced by up to one order of magnitude for HgCdTe and CdZnTe.\textsuperscript{215,217} In addition, the residual stress and strain in the crystal were also observed to be greatly reduced by proper annealing process.\textsuperscript{218-219} Thus, better crystallinity is expected after annealing. For BiI\textsubscript{3}, the temperature and time for annealing should be determined by characterizing the annealed crystal with EPD and X-ray rocking curve as there is no reported information available. The annealing atmosphere, either under vacuum, Argon gas, or I\textsubscript{2} vapor should also be experimentally determined.

6.2.5 Encapsulation of the Crystal

As indicated by XPS characterization, the surface of BiI\textsubscript{3} will be oxidized after a long time exposure in air. A proper encapsulation of the crystal and detector is therefore necessary to maintain the stability. HgL\textsubscript{2} is normally encapsulated in a Parylene or amorphous carbon film to prevent the sublimation in air.\textsuperscript{68} The same material could be applied for BiI\textsubscript{3} and should be tested in future work.

6.2.6 Surface Preparation

In this work, the surface of BiI\textsubscript{3} was prepared by cleaving the (001) planes, which was done by peeling off the top surface layers using Scotch tape. This will potentially cause the artifact of the surface morphologies and create variations from sample to sample. Post-growth surface treatment has long been established for HgL\textsubscript{2} and CZT
crystals during the detector fabrication to improve the electrode-material interface and reduce the leakage current. Various surface treatments including passivation of the surface,\textsuperscript{220} polishing,\textsuperscript{221} and chemical etching\textsuperscript{222} have been tested and evaluated before the finalized procedure was determined. Thus, a standard surface preparation procedure should be proposed and tested for Bil\textsubscript{3} surface in future. The work should start with a similar surface treatment to Hgl\textsubscript{2}. 
APPENDIX A
PURIFICATION OF BISMUTH IODIDE POWDER

A.1 Introduction
As discussed in chapter 4, the commercial powder was found to have high impurity concentration up to $10^{17}$ cm$^{-3}$. The impurities are deteriorative to the performance of the detector as they work as charge trapping center. The impurities also reduce the resistivity of the crystal. This appendix discusses the efforts of purifying the commercial BiI$_3$ powder using sublimation and vertical zone-melting method respectively.

A.2 Experiment Procedures
For sublimation process, 20 g commercial BiI$_3$ powder was vacuum sealed in a 16” long Pyrex glass ampoule. The ampoule was pre-cleaned as described in chapter 3. The sublimation was conducted in a 3-zone horizontal furnace with only two zones utilized. The hot zone was set at 330°C and the cold zone at 250°C. For vertical zone-melting process, 40 g commercial BiI$_3$ powder was vacuum sealed in a Pyrex glass ampoule and placed in the vertical furnace. The zone refinement was conducted at 460°C with a speed of 2 cm/h down the length of the ingot. Ten passes were repeated for the purification process.

A.3 Results and Discussion
A.3.1 Sublimation
The powder was completely sublimed after 24 hours. It was observed that BiI$_3$ polycrystalline slabs evenly deposited through a 12” long range inside the ampoule (Figure A-1). The sublimed crystals were divided into three segments with 4” long each. They were named as front, middle, and end segment with increasing distance from the
source. A small portion of the crystals were taken from each segment and subjected to ICP-AES for impurity analysis.

Figure A-1. BiI$_3$ powder in Pyrex ampoule after sublimation.

The measured impurity concentrations are summarized in Table A-1. It was observed that Cu and Fe were purified by sublimation, while Ag, Ni, and Si did not show appreciable concentration variation across the whole sublimation length thus they are hard to be purified by sublimation. The front segment showed the highest Cu and Fe concentration, which suggested that Cu and Fe tended to condense at higher temperature.

Table A-1. Impurity concentrations of commercial BiI$_3$ powder before and after sublimation (ppm).

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Pb</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before sublimation</td>
<td>3.4±0.60</td>
<td>0.8±0.02</td>
<td>7.1±1.86</td>
<td>0.1±0.01</td>
<td>&lt;1</td>
<td>7.2±0.71</td>
</tr>
<tr>
<td>Purified (front)</td>
<td>4.5±0.72</td>
<td>0.9±0.04</td>
<td>10.2±1.21</td>
<td>0.3±0.02</td>
<td>&lt;1</td>
<td>6.7±0.83</td>
</tr>
<tr>
<td>Purified (middle)</td>
<td>3.2±0.70</td>
<td>0.6±0.02</td>
<td>6.5±0.85</td>
<td>0.2±0.02</td>
<td>&lt;1</td>
<td>7.1±0.52</td>
</tr>
<tr>
<td>Purified (end)</td>
<td>4.2±0.43</td>
<td>0.5±0.02</td>
<td>8.3±1.05</td>
<td>0.2±0.01</td>
<td>&lt;1</td>
<td>6.8±0.61</td>
</tr>
</tbody>
</table>

A.3.2 Vertical Zone-melting

The ingot after zone-melting was cut to several 10 mm segments. A small amount of BiI$_3$ crystal (several mg) was taken from the central portion of each segment and dissolved in 10% trace-metal grade hydrochloric acid (HCl) to form a 10 mg/mL solution for ICP-AES measurement. The measured concentration for each impurity element is shown in Figure A-2.

It was observed that Ni and Pb were not purified by zone melting. The Fe impurity was pushed from the top of the ingot to the bottom. The other impurity elements
including Cu, Ag, and Si had the reverse concentration distribution. They had the highest impurity concentration at the top and the lowest at the bottom. The result suggested that the segregation coefficient ($C_s/C_L$) for Fe is less than 1, while Cu, Ag, and Si have segregation coefficient higher than 1. In other words, Fe has higher solubility in liquid Bi$_3$I$_3$ while Cu, Ag, and Si have higher solubility in solid Bi$_3$I$_3$. This indicated that the impurities cannot be purified simultaneously by just performing zone-melting process. However, a combination of this method with sublimation could potentially achieve a high level purification. Zone-melting could be used to purify Cu, Ag, and Si first. Then the purified ingot is sublimed to purify the Fe impurity. The sublimation should be conducted more than once to achieve better purification.

![Graph](image)

**Figure A-2.** Impurity concentrations of Bi$_3$I$_3$ powder after vertical zone-melting refinement.

**A.4 Summary and Conclusions**

Through sublimation and vertical zone-melting processes, it was observed that sublimation is useful to purify Cu and Fe, and vertical zone-melting is useful for Cu, Fe, Ag, and Si. However, Fe cannot be purified simultaneously with Cu, Ag, and Si for zone-refinement due to their different segregation coefficients. A combination of
sublimation and vertical zone-melting will be the best solution to purify BiI₃ single crystal.
APPENDIX B
GROWTH OF BISMUTH IODIDE CRYSTAL WITH DIFFERENT DIAMETERS

B.1 Introduction

The growth of BiI$_3$ single crystal with 0.75" diameter by MVB method has been discussed in chapter 3. As large volume crystal is desired for the application of gamma-ray detector, this appendix presents the attempts to grow BiI$_3$ single crystals of 1" and 1.25" diameters using MVB method. The single crystal with 0.5" diameter was also grown using the same methodology.

B.2 Experimental Procedures

The relationship between the temperature gradient and crystal diameter has been described in equation (3-4), which indicates that the temperature gradient $G_s$ is proportional to the square root of $(1/r)$, where $r$ is the crystal radius. It is also shown in equation (3-1) that at equilibrium, the growth rate is proportional to the temperature gradient if the radial gradient is ignored. In this study, the growth conditions for growing 0.75" diameter crystal were selected as the reference. The detailed temperature gradient and growth rate were selected as 10$^\circ$C/cm and 0.5 mm/h. The initial growth conditions for other diameters were determined based on equation (3-1) and (3-4), as shown in Table B-1. It is shown that for larger diameter crystal growth, both temperature gradient and growth rate should be lower. Physically, this means that at larger diameter, the temperature gradient is lowered to reduce the amount of the heat that need to be conducted away. The growth rate is also decreased to give more time for the crystal to conduct away the increased amount of heat due to the crystallization of more crystals.
Table B-1. Growth conditions for growing BiI$_3$ crystals with different diameters.

<table>
<thead>
<tr>
<th>Crystal Diameter (inch)</th>
<th>Growth Conditions</th>
</tr>
</thead>
</table>
|                        | Temperature gradient ($^\circ$C) | Growth rate (mm/h)  
| 0.75                   | 10               | 0.5               |  
| 0.5                    | 12.2             | 0.61              |  
| 1                      | 8.7              | 0.44              |  
| 1.25                   | 7.7              | 0.39              |  

B.3 Results and Discussion

It was observed that 0.5” diameter single crystal was successfully grown. The grown crystal rod and cleaved crystal (001) surface are shown in Figure B-1. However, the crystal growth for 1” and 1.25” diameters ended up with polycrystalline.

![Figure B-1](image)

Figure B-1. BiI$_3$ single crystal with 0.5” diameter. (a) the as grown crystal rod, and (b) cleaved single crystal (001) surface.

It is noticed that equation (3-4) overestimates the temperature gradient. In addition, the radial gradient may not be ignored anymore at larger crystal diameter. Equation (3-1) should be corrected as

$$\rho_s LR = K_s G_s - K_r G_r + K_r G_r$$ (B-1)

where $K_r$ and $G_r$ is the radial thermal conductivity and temperature gradient respectively. Thus the growth rate could be higher than the initial value. Based on the above discussion, the temperature gradient for growing 1” diameter crystal was reduced to 8$^\circ$C/cm, and the growth rate was increased to 0.5 mm/h. The growth still ended up with polycrystalline. Due to the unavailability of the thermal properties of BiI$_3$, the growth conditions are hard to be estimated and tested. It is impossible to try out every growth
condition for the sake of time. Beside growth condition, the stress induced by gravity force could also cause the failure of the crystal growth. As discussed in 6.2.1, the stress at the tip area is already very large for the 0.75" diameter crystal. When the crystal diameter increases, the stress could increase even more and cause serious slip at the growth face. A tilted growth should be set up to grow the large diameter crystal and verify this assumption.

B.4 Summary and Conclusions

Through theoretical deduction, the growth conditions for growing BiI$_3$ single crystals at different diameter have been determined. Single crystal was only successfully grown for a smaller diameter of 0.5". The crystal growth was failed for the larger diameters of 1" and 1.25". It was proposed that the growth conditions may not be correctly determined. Stress induced by gravity force could also account for the failure of the crystal growth.
APPENDIX C
TEM SAMPLE PREPARATION BY FOCUSED ION BEAM

C.1 Introduction

It is of interest to characterize the microstructure of the grown single crystals by transmission electron spectroscopy (TEM). The general sample preparation can be done through mechanical polishing, chemical etching, and focused ion beam (FIB). As BiI$_3$ reacts with H$_2$O, mechanical polishing and chemical etching are not suitable for BiI$_3$. Thus FIB becomes the only way to prepare TEM sample of BiI$_3$. This appendix discusses the efforts of preparing TEM sample using FIB technique.

C.2 Experimental Procedures and Results

As BiI$_3$ is highly sensitive to ion beams, the standard auto-FIB procedure is not applicable for it. Manual operation has to be used to avoid the damage to the sample. After a series of tries, a standard procedure has been determined for BiI$_3$. The FIB was always conducted at an ion beam voltage of 30 kV. The sample was sputter coated with a thin film of carbon before performing FIB. The detailed procedure is described as follows:

- The sample was tilted to 53°. A Pt layer with dimension of 20 x 3 x 1 μm (x, y, z) was deposited on top of the sample to protect it from ion beam damage. The ion beam current for deposition is 300 pA. The surface after Pt deposition is shown in Figure C-1.
Figure C-1. Pt deposition.

- Surface carbon layer was removed at ion beam current of 3000 pA with $z = 0.1 \, \mu m$.

Figure C-2. Carbon layer removal.

- Trenches were cut on both sides of the Pt layer at ion beam current of 1000 pA with $z = 0.3 \, \mu m$. 

Figure C-3. Formation of trench.

- The sample slab was thinning down to 1 μm at ion beam current of 300 pA.

Figure C-4. Thinning down to 1 μm.

- The sample slab was further thinning down to 0.3 μm at a smaller ion beam current of 50 pA.
Figure C-5. Thinning down to 0.3 μm.

- The sample was tilted to 7° to perform undercut. The ion beam current was 50 pA and z = 0.1 μm.

Figure C-6. Undercut.

- Final thinning down the slab to 100 nm at ion beam current of 10 pA.
Figure C-7. Final thinning down to 100 nm.

It was observed that the sample slab crumbled/curved at either step 6 or 7, this always happened when BiI$_3$ was thinning down. It is possibly due to the vulnerability of BiI$_3$ to the ion beams.

C.3 Summary and Conclusions

The TEM sample preparation for BiI$_3$ was not successful. The sample was always destroyed at the last several steps due to the highly ion beam sensitivity of BiI$_3$. 
APPENDIX D
NKN TAPE FOR PIEZOELECTRIC TRANSFORMER

D.1 Introduction

As a side project from BiI₃ single crystal growth, initial efforts have been made to develop a piezoelectric transformer. This appendix discusses the experiment and initial results of synthesizing sodium potassium niobate (Na₀.₅K₀.₅NbO₅, NKN) powder and ceramic tape for the application of piezoelectric transformer. A prototype of transformer made from the NKN slab has been tested.

D.2 Experimental Procedures

Sodium potassium niobate (Na₀.₅K₀.₅NbO₅, NKN) powder was synthesized by conventional solid state method. The starting materials were reagent grade K₂CO₃ (99%, Alfa Aesar), Na₂CO₃ (99.5%, Alfa Aesar) and Nb₂O₅ (99.5%, Alfa Aesar). The raw powders were dried at 120°C for 24h to remove the moisture then weighed according to the stoichiometry. The powders were mixed and ball milled for 24h in anhydrous ethanol. The milled slurry was dried at 120°C overnight then ground by mortar and pestle followed by sieving through a 212 μm mesh. The powder was calcined at 850°C for 10h. The calcined powder was ground and sieved again then uniaxially pressed to a rectangular shape slab with dimension of 19 x 6 x 3 mm³. The slab was sintered at 1100°C for 2h.

The sintered slab was polished and applied Au electrode by sputter coating. The prototype transformer adopted a Rosen type configuration, as illustrated in Figure D-1. The slab was first poled along the longitudinal direction then transverse direction, at 150°C under electric field of 1.7 kV/mm for 30 min. To test the performance of the transformer, it was connected to an Agilent 33220A wave generator at the input side.
and a multimeter at the output side. The wave generator can provide an alternative signal with frequency from 1 μHz to 20 MHz and amplitude up to 10 V.

![Figure D-1. Rosen type configuration of prototype NKN transformer.](image)

Attempts have been made to produce NKN thin slides using tape casting technique. The tape casting slurry was made according to the following procedures. The calcined NKN powder obtained from solid state process was dried at 120°C for 24h. Fish oil (2 wt%) was weighed and dissolved in the toluene (12 wt%), and the mixture was added to the ball mill. Anhydrous ethanol (12 wt%) was weighed and added to the ball mill. The dried NKN powder (59 wt%) was weighed and added to the mill. The mixture was ball milled for 24h. Butylbenzyl phthalate (5 wt%), polyvinyl butyral (5 wt%), and polyethylene glycol (5 wt%) were weighed and added to the ball mill. The final mixture was ball milled for an additional 24h. The slurry was poured to a beaker and de-aired at 0.8 atm vacuum for 10 min. The materials and their compositions are listed in Table D-1.

### Table D-1. Batch formulation of tape casting slurry of NKN

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition (wt%)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>NKN powder</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>Menhaden fish oil, blown Z-3</td>
<td>2</td>
<td>dispersant</td>
</tr>
<tr>
<td>Toluene</td>
<td>12</td>
<td>Solvent</td>
</tr>
<tr>
<td>Anhydrous ethanol</td>
<td>12</td>
<td>Solvent</td>
</tr>
<tr>
<td>Butylbenzyl phthalate, S-160</td>
<td>5</td>
<td>Plasticizer</td>
</tr>
<tr>
<td>Polyvinyl butyral, B-98</td>
<td>5</td>
<td>Binder</td>
</tr>
<tr>
<td>Polyethylene glycol, 8000</td>
<td>5</td>
<td>Plasticizer, binder</td>
</tr>
</tbody>
</table>
The slurry was tape-casted on Mylar sheet using a doctor blade. The tape was covered and dried in air overnight. To sinter the tape, it was heated to 600°C with a ramp rate of 0.3°C/min then hold for 6h. During this stage, the polymer component in the tape was burned out. The slow ramp rate will prevent the formation of crack due to the removal of water and polymer component. After burning out, it was heated to 1100°C with a ramp rate of 4°C/min then hold for 3h. The sintered tape was cooled to room temperature with a ramp rate of 4°C/min.

D.3 Results and Discussion

D.3.1 X-ray Diffraction

The XRD pattern of calcined and sintered NKN is shown in Figure D-2, which indicates that phase pure NKN was formed after calcination and the sintered slab was phase pure also. The sintered NKN slab has a dimension of 16.34 x 5.38 x 2.68 mm³ with density of 4.26 g/cm³, which is 95.4% of the theoretical density of 4.46 g/cm³.

![Figure D-2. XRD pattern of calcined and sintered NKN.](image-url)
D.3.2 Transformer Test

The equivalent circuit for a Rosen type piezoelectric transformer is shown in Figure D-3.\textsuperscript{223} The resonant frequency is strongly dependent on the load. The output to input voltage ratio is also a complicated function and dependent on the load. For a very large load resistance (open circuit), this ratio is approximately proportional to the mechanical quality factor $Q_m$ and electromechanical coupling factors:\textsuperscript{224}

$$
\frac{V_{out}}{V_{in}} \propto k_{31} k_{33} Q_m L / t
$$

(D-1)

where $k_{31}$ and $k_{33}$ are the transverse and longitudinal electromechanical coupling factors, $L$ and $t$ are the length and thickness of the transformer, respectively.

The NKN transformer tested in this study has a dimension of 14.01 x 4.72 x 2.12 mm\textsuperscript{3}. The operating frequency was calculated to be $F = c/4L = 12153$ Hz according to Fuji & Co. Piezo Science, where $c$ is velocity of sound. The input voltage was 10 V peak to peak at 12153 Hz. The output voltage was measured with or without load. The tested loads have resistance of 100 $\Omega$, 1.5 k$\Omega$, and 5.6 M$\Omega$. At 12153 Hz operating frequency, 5 V output voltage was measured without load. The output voltage with loads was measured to be 5 V, 3.2 V and 0 with corresponding load of 5.6 M$\Omega$, 1.5 k$\Omega$, and 100$\Omega$. The operating frequency was also changed from 1 kHz to 300 kHz with step of 10 kHz. The output voltage kept at 5 V without load. Clearly there is problem with our prototype transformer since the output voltage is not amplified at all. Possible reason is that the working frequency is not even close to the resonant frequency, which was not calculated in this study due to lack of the information of the piezoelectric properties. Another possible reason is that the material was not completely poled since the electric field for poling NKN is normally reported to be 3 kV/mm and above.\textsuperscript{224-226}
while in this study 1.7 kV/mm was used to pole the material due to the limitation of the equipment.

Figure D-3. Equivalent circuits of a piezoelectric transformer: (a) general model, (b) after reflecting the output capacitance and load resistance to the primary, and (c) after parallel to series transformation. (After Ivensky et al.223)
D.3.3 Tape Casting

The casted tape has a thickness of around 0.2 mm. It has been successfully sintered without crack and bending. Figure D-4 shows a pre-sintered tape which is casted on a Mylar sheet.

Figure D-4. NKN tape casted on a Mylar sheet.

D.4 Summary and Conclusions

Phase pure NKN powder has been successfully prepared by solid state processing. The calcinations was conducted at 850°C for 10 h. NKN slab was sintered at 1100°C for 2 h and determined to be phase pure by XRD. The initial test on the prototype piezoelectric transformer was not successful. It is probably due to the wrong working frequency or the poor poling. NKN tape with thickness of around 0.2 mm has been successfully prepared and sintered at a very careful temperature program.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Wei Qiu was born in 1975 in Chongqing, China. He obtained his B.S. degree in materials science and engineering at Tsinghua University, Beijing, in 1999. After graduation, he was offered a research position in the state key laboratory of fine ceramic and processing at Tsinghua University, where he was in charge of the development of a ceramic-polymer frictional material for the application in the ultrasonic motor. In 2000, he began his Master’s study in Dr. Huey H. Hng’s research group in department of materials science and engineering at Nanyang Technological University (NTU), Singapore. His study focused on the microstructural and piezoelectric properties of lead zirconate titanate (PZT) near the morphotropic phase boundary. In 2002, He received his Master’s degree and joined Dr. Ooi K. Tan’s group as a research assistant in department of electrical and electronic engineering at NTU. His research focused on the synthesis of barium strontium titanate (BST) thin film by sol-gel process and developing the BST thin film for bio-sensing application. In 2005, he began his Ph.D. study in Dr. Juan C. Nino’s research group. His Ph.D. study focuses on the single crystal growth of BiI₃ by modified vertical Bridgman technique for the application of room temperature gamma-ray detector. After spending 5 years at UF in Gainesville, he received his Ph.D. from the University of Florida in the summer of 2010.