GROWTH AND CHARACTERIZATION OF BISMUTH SELENIDE THIN FILMS BY CHEMICAL VAPOR DEPOSITION

A Dissertation in
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by
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ABSTRACT

Topological insulators are a recently discovered class of materials that have garnered much interest due to their unique surface states. With its relatively high band gap (0.3eV) and nearly ideal band structure, Bi$_2$Se$_3$ has been a primary material of interest in the study of topological insulating behavior. However, several factors have made this study difficult. Bi$_2$Se$_3$ typically has a high native selenium vacancy concentration, and selenium vacancies act as donors in the material, leading to a high bulk electron concentration. The surface of Bi$_2$Se$_3$ has also been shown to be susceptible to environmental doping when exposed to ambient air. Combining these two factors means that Bi$_2$Se$_3$ is usually highly n-type doped, making it difficult to study the surface conducting states by transport measurements.

This study investigated the use of two different chemical vapor deposition (CVD) techniques for the growth of Bi$_2$Se$_3$ thin films on sapphire (001): hybrid physical-chemical vapor deposition (HPCVD) and metal-organic chemical vapor deposition (MOCVD). HPCVD is a process which combines the evaporation of elemental selenium with the thermal decomposition of trimethylbismuth (TMBi). The use of elemental selenium immediately around the substrate provides a high overpressure of selenium, allowing for reduction of the selenium vacancy concentration. Bi$_2$Se$_3$ films grown on sapphire were epitaxial and highly oriented parallel to the substrate giving rise to narrow X-ray rocking curves (full-width-at-half-maximum=160 arcsecs for (006) reflection) and 6-fold rotational symmetry as determined by phi scans. The structural properties were consistent with deposition via a van der Waals epitaxy process. The selenium to bismuth
ratio (VI/V) ratio proved important for achieving a reduced electron concentration of $<8 \times 10^{18}$ cm$^{-3}$ and room temperature mobilities of up to 800 cm$^2$V$^{-1}$s$^{-1}$.

MOCVD growth of Bi$_2$Se$_3$ was also investigated using trimethylbismuth (TMBi) dimethylselenide (DMSe) as precursors. Epitaxial Bi$_2$Se$_3$ films were also produced by MOCVD on sapphire, however, the electron concentrations were generally higher (1-3x$10^{19}$ cm$^{-3}$) and the mobilities were lower (~250 cm$^2$V$^{-1}$s$^{-1}$) than films grown by HPCVD. This difference is likely due to the higher VI/V ratios more easily achievable with HPCVD growth compared to MOCVD growth. The primary advantage of MOCVD compared to HPCVD, however, was the flexibility that it afforded to grow multilayer structures. This was demonstrated through the deposition of Bi$_2$Se$_3$/MgB$_2$ heterostructures on sapphire for potential use in the study of proximity effect induced topological superconductivity.

The effects of different ambient environments on the surface chemistry and electrical properties of Bi$_2$Se$_3$ were also studied. Hall measurements performed over time in air, N$_2$, H$_2$O vapor, and O$_2$ ambient environments showed that the type of ambient gas has a significant impact on the electrical properties of Bi$_2$Se$_3$. Samples held in air and water vapor showed a 25-30% increase in carrier concentration over 10 hours, while a sample held in N$_2$ showed no increase. A sample held in O$_2$, however, showed an initial 20% decrease in carrier concentration followed by a steady increase with time eventually reaching a value 15% above the initial value after 10 hours. Water vapor was determined to be the major contributing factor to the oxidation of Bi$_2$Se$_3$ in air over time, reacting with the Bi$_2$Se$_3$ surface and leading to an increase in free electrons, increasing the carrier concentration. This was supported by x-ray photoelectron spectroscopy (XPS) showing
oxygen bonding on the surface for samples held in air and oxygen, but not in nitrogen. Angle resolved photoemission spectroscopy (ARPES) shows that nitrogen was able to suppress oxidation over a period of several weeks compared to a sample stored in air.
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Chapter 1
Introduction

1.1 Motivation

Topological insulators were first proposed theoretically in 2005\textsuperscript{1} and demonstrated experimentally in 2007\textsuperscript{2}. They have garnered much interest due to their unique electronic structure that is predicted to consist of insulating bulk states and protected metallic surface states that arise in materials with strong spin-orbit coupling.\textsuperscript{3} The presence of these conducting surface states was first confirmed experimentally in 2008.\textsuperscript{4}

With potential applications in spintronics, the most prominent use of topological insulators may be for the realization of Majorana fermions. Majorana fermions are fermions which are their own antiparticles.\textsuperscript{5} While no fundamental particles have been shown to be Majorana fermions, quasiparticles which behave in the same way, called Majorana bound states, have been predicted to exist at the interface of a superconductor with a topological insulator.\textsuperscript{6} Due to the proximity effect, Cooper pairs from the superconductor can tunnel into the topologically protected surface states of the TI material at an interface between the two materials.\textsuperscript{7} Since the pair making up a Majorana quasiparticle are spatially separated, they are protected from most types of decoherence.\textsuperscript{8} Their unique properties could then possibly be harnessed for novel devices such as a fault-tolerant topological quantum computer.\textsuperscript{9}
Bi$_2$Se$_3$ has been a primary material of interest for studying topological insulating behavior. This is due to its nearly-ideal band structure$^{10}$ and relatively high band gap energy (0.3eV).$^{11}$ High quality bulk Bi$_2$Se$_3$ crystals have been fabricated from a stoichiometric melt of Bi and Se$^{12}$ and studies have been performed with thin films exfoliated from these bulk crystals.$^{13}$ However, further advances in the study and application of topological insulator materials requires the ability to form highly-oriented Bi$_2$Se$_3$ films directly on substrates of interest such as sapphire and silicon and on superconducting materials.

The electrical properties of Bi$_2$Se$_3$ are also a concern for topological insulator studies. Bulk Bi$_2$Se$_3$ crystals have been fabricated with background electron concentrations in the $10^{17}$ cm$^{-3}$ range,$^{14}$ however, thin films have generally had carrier concentrations almost two orders of magnitude higher, in the range of $10^{19}$-$10^{20}$ cm$^{-3}$. The n-type conductivity is generally attributed to native defects, in particular selenium vacancies, which are prevalent in Bi$_2$Se$_3$. The high background electron concentration acts as a parallel conduction path in transport measurements which makes it difficult to isolate the behavior of the topological surface states. Several methods have been pursued to circumvent this problem including the addition of compensating impurities such as Ca$^{15}$ and Sb$^{16}$ and the use of gated electrical test structures which are used to deplete carriers from the bulk of the film.$^{17}$ However, there is significant interest in the development of methods to reduce the n-type conductivity in Bi$_2$Se$_3$ films without the need for additional dopants or specialized test structures.

To date, thin films of Bi$_2$Se$_3$ have been fabricated primarily by molecular beam epitaxy (MBE). Thanks to its ultrahigh vacuum operating pressure and high purity, MBE
is able to produce high quality Bi$_2$Se$_3$ films. Films were typically grown at temperatures from 200-250°C, while higher growth temperatures lead to significantly increased carrier concentration$^{18}$ and irregular 3D island growth rather than layer by layer growth.$^{19}$ Films grown by MBE typically show c-axis orientation with 6-fold rotational symmetry.$^{20}$ Hall mobility at low temperature (<30K) has reached the 6000 cm$^2$V$^{-1}$s$^{-1}$ range, but the bulk carrier concentrations remains on the order of 1x10$^{19}$ cm$^{-3}$.$^{21}$

An additional problem encountered in handling and processing Bi$_2$Se$_3$ thin films is the reactivity of the surface with ambient air which alters the electronic properties of the material. Previous studies have shown a significant increase in the electron concentration and reduction in mobility of the films upon exposure of the samples to air.$^{22}$ This is of great concern for the study of the topological surface states since this change arises from an accumulation of negative charge resulting in band bending at the surface as determined by angle-resolved photoemission spectroscopy (ARPES), a surface sensitive technique.$^{23}$ The formation of oxides upon exposure to air has also been reported.$^{24}$

1.2 Focus of This Study

The main goal of this study was to investigate the use of chemical vapor deposition (CVD) for the synthesis of Bi$_2$Se$_3$ films. CVD is typically carried out at much higher pressures (10-760 Torr) than MBE (10$^{-10}$ Torr), consequently, the gas phase selenium partial pressure is much higher in a CVD environment which may be beneficial for reducing the selenium vacancy concentration and thereby the n-type conductivity of
Bi$_2$Se$_3$. Two different CVD techniques were investigated in this study: hybrid physical-chemical vapor deposition (HPCVD) and metal-organic chemical vapor deposition (MOCVD).

Hybrid physical-chemical vapor deposition (HPCVD) is a deposition technique which combines thermal decomposition of a chemical precursor in conjunction with evaporation of an elemental source in close proximity to the growth substrate. It has previously been used to grow MgB$_2$, a superconducting material which requires a high gas phase partial pressure of Mg in order to achieve stable film growth. This high vapor pressure ratio is easily attainable using HPCVD, which uses a solid source Mg source in close proximity to the substrate in combination with the thermal decomposition of Bi$_2$H$_6$. The HPCVD method is particularly relevant to the growth of Bi$_2$Se$_3$ because a higher selenium/bismuth (VI/V) ratio has been shown to be beneficial for reducing the selenium vacancy concentration, which in turn lowers the carrier concentration. In this study, a metalorganic bismuth source (trimethylbismuth (TMBi)) was used in conjunction with evaporated elemental selenium in an effort to achieve a high VI/V ratio during growth. In the HPCVD reactor, selenium pellets are placed on the same heated susceptor as the substrate to ensure a high local partial pressure. The disadvantage of this configuration is that it is not possible to independently control the temperatures of the selenium source and the substrate which reduces the process flexibility. In addition, the substrate temperature was limited to temperatures near the melting point of selenium (220°C) to prevent rapid evaporation of the selenium during growth. The low substrate temperature resulted in inefficient decomposition of the TMBi source. As a result, a two heater setup was used (see section 3.3.1) in which an additional resistance heater was
placed upstream in the reactor to promote the decomposition of TMBi while maintaining a low substrate/selenium source temperature. The effects of varying the two heater temperatures, which varies the VI/V ratio, and the pressure on the structural and electrical properties of Bi$_2$Se$_3$ films deposited on sapphire were studied in depth.

As a result of the constraints placed on the substrate and source temperature in HPCVD growth, MOCVD was also investigated for the growth of Bi$_2$Se films. MOCVD growth was carried out using metalorganic precursors (trimethylbismuth (TMBi) and dimethylselenide (DMSe)) that were both supplied in the gas phase. MOCVD was previously used to a limited extent to grow thick polycrystalline Bi$_2$Se$_3$ for thermoelectric studies.\textsuperscript{27} It has the advantage over HPCVD of being able to control the substrate temperature completely independently of the source temperature and to use higher temperatures to grow other layers before or after the Bi$_2$Se$_3$ layer growth. The effects of process conditions (heater temperatures and other parameters such as the VI/V ratio and H$_2$ flow through the chamber) on film properties were studied. MOCVD also allows for the formation of heterostructures without exposure to air. While HPCVD would require opening the reactor chamber and adding the selenium source in between the growth of two different layers, MOCVD allows the sequential growth of multiple materials without the need to open the reactor chamber. This allows for the creation of MgB$_2$/Bi$_2$Se$_3$ bilayer structures, allowing for the study of proximity effect induced superconductivity in Bi$_2$Se$_3$.

The reaction of Bi$_2$Se$_3$ films in air over time is of great concern for film characterization and processing. Similar to prior reports, it was found that the electron concentration of the Bi$_2$Se$_3$ films grown by HPCVD increased after removal from the
growth chamber and exposure to ambient air. In an effort to better understand this environmental doping effect, time-dependent Hall-effect measurements were carried out on the Bi$_2$Se$_3$ films under various ambient environments (air, N$_2$, H$_2$O vapor, and O$_2$). X-Ray photoelectron spectroscopy (XPS) was used in combination with the Hall measurements to correlate chemical changes on the surface with measured changes in conductivity.

1.3 Organization of the Thesis

In Chapter 2, the relevant literature is reviewed, focusing on the background of topological insulators and the interest in Bi$_2$Se$_3$ in particular. Previous growth of Bi$_2$Se$_3$ using both MBE and MOCVD is discussed along with the growth mechanism of Bi$_2$Se$_3$, its reactions in air, and the previous utilization of HPCVD for MgB$_2$ growth. Chapter 3 describes the experimental procedures used for both HPCVD and MOCVD and the growth systems utilized. The techniques used to characterize the films are also discussed, particularly Hall measurements and X-ray diffraction. The methods used to study the effects of different ambient environments on Bi$_2$Se$_3$ will also be explained, particularly Hall measurements over time. Chapter 4 discusses the HPCVD growth technique. The structural and electrical properties of films grown with varying conditions, mainly the evaporation temperature of Se, the decomposition temperature of TMBi, and pressure, will be discussed in depth. Chapter 5 focuses on the MOCVD growth of Bi$_2$Se$_3$ thin films and its optimization by varying the substrate temperature, flow rates, and the selenium to bismuth ratio. Chapter 6 discusses the effects of different ambient
environments on the electrical properties and surface bonding of Bi$_2$Se$_3$ films. Finally, Chapter 7 summarizes all these findings and discusses possibilities for future work in this area.
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Chapter 2
Literature Review

2.1 Topological Insulators

2.1.1 Introduction

Topological insulators (TI) are materials different in type from conventional insulators. A conventional insulator is a material where the Fermi energy lies in the middle of the gap between the maximum of the valence band and the minimum of the conduction band (Figure 2-1a). The thing that differentiates this conventional insulator from a conductor is the position of the Fermi level. However, a material with strong spin-orbit coupling (SOC) can have topological “twisting” in the band structure. At boundaries, this can cause a crossover of the valence and conduction bands. If this crossover happens an even number of times, this is topologically equivalent to a conventional insulator (Figure 2-1c). However, if the crossover happens an odd number of times, this forms a topologically distinct material known as a topological insulator (Figure 2-1b). The crossover in the surface states allows spin-dependent conduction along the boundary even in a bulk insulator. Because of the nature of these spin-dependent conduction channels, backscattering in the absence of a magnetic impurity which could change an electron’s spin is theoretically forbidden.
2.1.2 First Topological Insulators

The first topological insulators theorized were 2D systems with 1D boundaries (edges). HgTe quantum wells were the first concrete example of this type of system which was predicted and fabricated. BiSb was predicted as the first identified 3D topological insulator with 2D edge boundary states, confirmed by angle-resolved photoemission spectroscopy (ARPES) measurements. Unfortunately, the surface structure of BiSb is relatively complicated.
with a small band gap.\textsuperscript{6} But Bi\textsubscript{2}Se\textsubscript{3}, Bi\textsubscript{2}Te\textsubscript{3}, and Sb\textsubscript{2}Te\textsubscript{3} were then predicted to be 3D topological insulators, opening up the possibly of observing TI behavior at room temperature.\textsuperscript{7}

2.2 Growth of Bi\textsubscript{2}Se\textsubscript{3}

2.2.1 Why it is preferred?

Bismuth selenide has emerged as the primary 3D topological insulator of interest for growth and analysis. This is due to three primary reasons: 1. The band structure of Bi\textsubscript{2}Se\textsubscript{3} forms a nearly-ideal Dirac cone compared to topological insulators with much more complicated structures such as BiSb.\textsuperscript{8} 2. Bi\textsubscript{2}Se\textsubscript{3} is a stoichiometric material. This means that it can theoretically be produced with higher purity and less disorder than an alloy compound.\textsuperscript{8} 3. Bi\textsubscript{2}Se\textsubscript{3} has a bulk band gap of 0.3eV. This distinguishes it as having the largest bulk band gap of any 3D topological insulator.\textsuperscript{9} This relatively large band gap means that topological insulating behavior can theoretically be seen at room temperature. This is essential for potential applications.

Also important is its crystal structure, which is made up of alternating layers of bismuth and selenium atoms with the basic repeating unit made up of five alternating layers Se-Bi-Se-Bi-Se. While the five individual layers of Bi and Se atoms that make up a quintuple layer (0.95 nm thick) are held together with strong covalent bonding, the bonding between layers consists of weak van der Waals bonds (Figure 2-2).\textsuperscript{10} Since the
quintuple layers are terminated by weak van der Waals bonding, this means that chemical bonds are not formed at an interface with another material.\textsuperscript{11}

\textbf{Figure 2-2. Crystal structure of Bi$_2$Se$_3$, made up of alternating layers of Se and Bi atoms.}\textsuperscript{12}

\textbf{2.2.2 Bulk Crystal Growth}

Growth of bulk crystals and then exfoliation of thin layers from these crystals has been used for the study of the topological insulator properties of Bi$_2$Se$_3$.\textsuperscript{13} The process generally involves heating a stoichiometric ratio of elemental bismuth and selenium
powders in a sealed ampoule to roughly 800°C for a period of several hours, stirring it, and allowing it to crystallize by slowly cooling to room temperature.\textsuperscript{14}

2.2.3 MBE

Molecular beam epitaxy (MBE) has been the primary method of fabricating thin films of Bi\textsubscript{2}Se\textsubscript{3} for topological insulator studies. MBE takes place at ultra-high vacuum conditions ($<10^{-10}$ torr). Precursors are elemental sources held in heated Knudsen cells. When the sources are opened up to the substrate, the precursor atoms flow in a “beam” to the substrate due to the very low pressures causing very little diffusion.

2.2.3.1 Advantages and Disadvantages

The primary advantages of MBE are purity and precision. Due to the very low growth pressure and high purity elemental sources, films with high chemical purity can be produced. Also, due to low growth rates and \textit{in situ} measurements such as reflection high-energy electron diffraction (RHEED), films of precise thickness and composition can be grown. Also, growth can generally take place at lower temperatures than CVD because no precursors have to be thermally decomposed.

The disadvantages of MBE have the same origin as the advantages. The very low growth pressures and slow growth rates lead to long pump down times and low throughput. MBE is also costly to maintain.
2.2.3.2 Previous Growth

MBE growth of Bi₂Se₃ has been performed on a variety of substrates (see section 2.4). Substrate temperatures of around 200-250°C were found to be crucial for high quality growth. At higher temperatures, the carrier concentration increased significantly due to a higher selenium vacancy concentration. Higher temperatures (>300°C) also promoted 3D island growth as opposed to layer-by-layer growth. On the other hand, too low of a growth temperature can result in polycrystalline film growth due to insufficient energy for surface diffusion.

Another important aspect to control in growth has been the Se/Bi (VI/V) ratio. A VI/V flux ratio of 5-20 has been typical. Because of the tendency to form Se vacancies and the possibility of forming Bi-rich phases, ratios much higher than the stoichiometric ratio are used. At VI/V ratios higher than 20, anti-site and interstitial Se point defects may form.

2.2.4 MOCVD

Metal-organic chemical vapor deposition (MOCVD) has previously been used for the deposition of Bi₂Se₃ thin films to a limited extent. MOCVD is a subset of CVD in which the precursors are metal-organic molecules, metal atoms bonded to small organic groups such as methyl and ethyl groups. These precursors have significantly higher vapor pressures than the metal constituents and are often in a liquid phase at room temperature. A carrier gas is used to transport the metal-organic vapor to the growth
chamber where they decompose at elevated temperature. This method has been used to fabricate a variety of semiconductor compounds including InP, GaN, and ZnSe.

2.2.4.1 Advantages and Disadvantages

MOCVD has a few advantages over MBE. First of all is its significantly higher throughput. This is due primarily to the very low growth pressures required for MBE ($<10^{-10}$ torr), compared to 10-600 Torr for MOCVD. This greatly reduces the pump down times required for MOCVD compared to MBE. Specifically for $\text{Bi}_2\text{Se}_3$, these higher pressures result in a higher vapor pressure of selenium over the film, which may help minimize the selenium vacancy concentration. MOCVD also typically has higher growth rates than MBE, with typical MBE growth rates of around 2 nm/min for $\text{Bi}_2\text{Se}_3$ and around 5-10 nm/min or more for MOCVD.

Since MOCVD does not use pure elemental precursors, but instead metal-organic molecules, carbon contamination can be a concern.

2.2.4.2 Previous Growth

MOCVD has only seen very limited use in the growth of $\text{Bi}_2\text{Se}_3$. A single group at Montpellier 2 University in France investigated MOCVD growth of $\text{Bi}_2\text{Se}_3$ for use as a thermoelectric. Using trimethylbismuth (TMBi) and two different selenium precursors, diethylselenide (DESe) and ditertbutylselenide (DTBSe), they grew polycrystalline $\text{Bi}_2\text{Se}_3$ thin films on pyrex substrates. The best growth conditions produced...
polycrystalline films with a carrier concentration of $\sim 2 \times 10^{19} \text{cm}^{-3}$ and Hall mobility of 330 cm$^2$V$^{-1}$s$^{-1}$. Films grown with DTBSe exhibited slightly lower carrier concentration and higher mobility than those grown by DESe. This was attributed to larger grain sizes for the DTBSe-grown films. Films grown using DTBSe were grown at slightly lower temperatures (450°C as opposed to 475°C) because DTBSe decomposes at lower temperatures than DESe.$^{23}$

2.3 Van der Waals Epitaxy

As mentioned in section 2.2.1, the crystal structure of Bi$_2$Se$_3$ consists of quintuple layers of alternating sheets of covalently-bonded Bi and Se atoms. Between these layers are weak van der Waals bonds. Other layered materials with similar bonding have been grown by van der Waals epitaxy. Van der Waals epitaxy has also been reported for the growth of Bi$_2$Se$_3$. $^{24}$

2.3.1 Layered Materials

Van der Waals epitaxy refers to the epitaxial growth of two 2D materials with weak van der Waals interplanar bonding. This method was first reported in 1986 for the growth of MoSe$_2$ on MoS$_2$. $^{25}$ Conventional epitaxy can only accommodate a very small lattice mismatch between the film and substrate before strain-relieving defects form. In conventional epitaxy chemical bonds also form between the substrate and film. In van der Waals epitaxy, the weak van der Waals bonding of many 2D materials allows for much
larger lattice mismatches to be accommodated, up to 50% and does not form chemical bonds at the interface.\textsuperscript{26} The weak bonding also leads to atomically sharp interfaces due to a lack of interfacial reactions.\textsuperscript{27} (Figure 2-3)\textsuperscript{28}

![Figure 2-3. (a) conventional epitaxy and (b) van der Waals epitaxy\textsuperscript{28}](image)

Two different film textures are seen in layered materials deposited by van der Waals epitaxy.\textsuperscript{29} Type I consists of platelets growing out perpendicular to the substrate. Type II, on the other hand, is layer-by-layer growth of c-axis oriented grains parallel to the substrate surface. Type II is greatly preferred and can result in high quality single crystal growth (Figure 2-4).
Figure 2-4. (a) Cross-sectional SEM image and (b) diagram showing type I misaligned growth. (c) Top-down SEM image and (d) diagram showing type II c-axis oriented growth.

2.3.2 Xenotaxy

Xenotaxy is the name given to the growth of a 2D layered material on a 3D material by van der Waals epitaxy. Similar flexibility in lattice matching can be seen as long as the surface of the 3D substrate is properly passivated.\textsuperscript{30} For instance, the 2D layered material GaSe has been grown on Si substrates in the (100), (110), and (111) orientations.\textsuperscript{31} All three GaSe films exhibited c-axis orientation. However, there is some interaction between the substrate and the layered film in that the surface crystal structure can act as a template for the deposited film in terms of the in-plane rotation. Thus, a hexagonal close packed (HCP) substrate surface acts as a template and orients the nucleating grains for the hexagonal films even with a large lattice mismatch.\textsuperscript{32} Thus, a non-HCP surface can accommodate a hexagonal layered material, but the nucleating
grains will not be as well-oriented. This is why Si (111) leads to preferred in-plane rotation in a deposited film, but Si (100) leads to randomly oriented in-plane rotation.\textsuperscript{33}

\textbf{2.3.3 Growth-Related Defects}

Van der Waals epitaxy has particular qualities that allow for the development of defects during growth. While the initial growth is dependent on the substrate, the weak van der Waals bonding which holds the quintuple layers together allows for the easy formation of twin boundaries and stacking faults. After the deposition of a single Se layer, two close-packed configurations of Bi atoms are possible. If these two configurations nucleate at two different sites, it will create a twin boundary where these regions meet.\textsuperscript{34} In addition to these, there are three possible non-equivalent orientations with which quintuple layers may stack on top of each other. Inconsistency in the stacking between layers leads to these twin boundaries, which are likely to form in terms of formation energy.\textsuperscript{34} Both of these types of defects can form independent of the substrate chosen.

Also of concern in the growth of Bi\textsubscript{2}Se\textsubscript{3} on different substrates is the formation of triangular pyramids on the surface due to pinning. When a quintuple layer, growing on a surface, meets a step edge, or some other pinning site, the growing layers “jumps” up the step, and because a certain growth direction is preferred, this process repeats, forming a pyramid-shaped structure and increasing the roughness of the surface (See Figure 2-5).\textsuperscript{35} Choosing a substrate that will minimize these pinning sites is important.
2.4 Substrates

While the van der Waals growth mechanism makes substrate selection less important than for conventional heteroepitaxy, it has still been shown to have a significant impact on film quality. Probably the most important feature in substrate selection is picking a substrate that will help to orient growing Bi$_2$Se$_3$ grains in-plane. Bi$_2$Se$_3$ grows c-axis oriented on many substrates. This is consistent with the van der Waals epitaxy growth mechanism. But, the grains may be randomly oriented in-plane resulting in a film with many grain boundaries that can degrade electrical properties.

Bi$_2$Se$_3$ has been successfully grown on a variety of substrates including Si(111),$^{36}$ GaAs(111)B,$^{37}$ SiC(0001),$^{38,39}$ CdS(0001),$^{40}$ InP (111),$^{41}$ and insulating substrates such as Al$_2$O$_3$(a-plane)$^{42}$ and SrTiO$_3$(111).$^{43}$ While growth on those substrates most closely
lattice matched to Bi$_2$Se$_3$, CdS (-0.24%) and InP (0.24%), showed the best structural properties, growth on substrates with a much larger lattice mismatch (such as Al$_2$O$_3$ (13.5%)) also resulted in c-axis oriented growth with the expected 6-fold in-plane rotational symmetry indicative of a well-oriented film. Another technique to ensure a properly oriented film and minimize twinning is to use a vicinal substrate. This has been used with mis-cut Si(111) to improve in-plane orientation and reduce carrier concentration by nearly an order of magnitude.

Another aspect of surface selection is proper surface passivation. As mentioned above, van der Waals epitaxy relies on weak van der Waals interactions between the substrate and film. If dangling bonds are present on the surface of the substrate, this can lead to irregular and out-of-plane growth.

A few techniques have been used to ensure proper passivation of the substrate surface. The first is to grow on a relatively inert substrate such as Al$_2$O$_3$ which would be relatively free of dangling bonds. For the most common substrate, Si (111), surface passivation normally involved terminating the dangling bonds with either hydrogen or selenium.

A last method that has been used to minimize the effect of dangling bonds on the substrate surface is a two-stage growth process. A thin layer of Bi$_2$Se$_3$ is deposited at low temperature, forming an amorphous layer. As the temperature is increased to the normal growth temperature, a crystalline layer forms and acts as a passivation layer.
2.5 Oxidation of Bi$_2$Se$_3$

Once the film is grown, degradation of the film surface in air is a significant concern. The electrical properties of Bi$_2$Se$_3$ thin films have been shown to be time-dependent in air with carrier concentration increasing and electron mobility decreasing with prolonged exposure to air due to band bending near the surface.$^{52}$ This has been attributed to extrinsic defects such as the incorporation of impurity atoms into lattice sites$^{53}$ and adsorption of gas impurities on the surface$^{54}$ and to oxidation$^{55}$.

The band bending results in an accumulation layer of negative charge at the surface. The accumulation layer, while independent of the topological surface states$^7$, must be distinguished from them in transport measurements to accurately characterize the surface states. Degradation, resulting in an increase in conductivity, has been seen in air$^{56}$, CO$^{57}$, H$_2$O$^{58}$, and O$_2$$^{59}$. H$_2$O in particular has been shown to induce surface states similar to those that develop in a sample cleaved in air then measured in vacuum.$^{58}$ On the other hand, O$_2$ has shown to be a p-type dopant$^{59}$, filling selenium vacancies, but in other studies has been shown to alter the surface states and decrease spin current.$^4$ A greater understanding of the exact mechanism of the reactions of Bi$_2$Se$_3$ in air must be achieved in order to develop methods to handle films for characterization and processing.

2.6 HPCVD

Hybrid physical chemical vapor deposition (HPCVD) has previously been used in the growth of MgB$_2$, a material which exhibits superconductivity at temperatures near 39K. Thin film growth proved difficult by normal CVD processes due to MgB$_2$’s
thermodynamic instability at temperatures needed for epitaxial growth.\textsuperscript{60} It was
determined that a relatively high Mg partial pressure was necessary for thermodynamic
stability at these high temperatures. Thus, in HPCVD, solid Mg pellets placed in close
proximity to the substrate act as the Mg source in order to supply this high vapor pressure
while $B_2H_6$ is used as a gas boron source.

This same method can potentially be used to reduce the carrier concentration in
$\text{Bi}_2\text{Se}_3$, which is caused by a high concentration of selenium vacancies acting as electron
donors.\textsuperscript{61} Thus in HPCVD of $\text{Bi}_2\text{Se}_3$, a gas Bi source is used in conjunction with solid
selenium pellets in close proximity to the substrate in order to give a high selenium-to-
bismuth (VI/V) ratio and thereby reduce the carrier concentration of $\text{Bi}_2\text{Se}_3$ thin films.

2.7 Literature Review Summary

Topological insulators are of interest due to their unique conducting surface states
in a bulk insulator. Both 2D and 3D TI materials have been predicted and fabricated.
Many TI’s failed to gain much interest due to their very small band gaps, which make
room temperature measurements and applications impossible. $\text{Bi}_2\text{Se}_3$, $\text{Bi}_2\text{Te}_3$, and $\text{Sb}_2\text{Te}_3$
have emerged as candidates for room temperature TI applications. $\text{Bi}_2\text{Se}_3$ is of the most
interest for three reasons. It has the highest band gap (0.3eV), which makes room
temperature applications possible, it has a near-ideal band structure, and its
stoichiometric nature theoretically allows a more ordered system with higher purity than
alloy systems.
Bi₂Se₃ has been previously fabricated using MBE and MOCVD. MBE offers the advantage of high purity and precision, but has very low throughput and is very costly. MOCVD, because of its higher growth pressures, can potentially achieve a higher partial pressure of selenium over the film and minimize the selenium vacancy concentration, but tends to have lower crystal quality. Carbon contamination from the metal-organic precursors is also a concern.

HPCVD has been previously used to grow MgB₂. MgB₂ needs a high vapor pressure of magnesium at the growth temperatures used because of thermodynamic instability. So, solid magnesium pellets immediately around the substrate are used with a gaseous boron source to create a very high vapor pressure of magnesium over the substrate surface. Due to the propensity of Bi₂Se₃ to include a high concentration of selenium vacancies, which lead to a high carrier concentration, this same method will be used with selenium pellets to create a high selenium to bismuth ratio in order to reduce the selenium vacancies.

Bi₂Se₃, being a layered material, grows by van der Waals epitaxy. Van der Waals epitaxy has an advantage over conventional epitaxy in that the weak van der Waals bonds between layers can accommodate very high lattice mismatches (>50%) without stress-relieving defects forming. Even so, substrate selection can have an impact on film quality. Hexagonal substrates help orient the film, leading to epitaxial growth with 6-fold symmetry in the film. Lower lattice-mismatched substrates tend to lead to higher film quality, but the effect is not nearly as pronounced as in conventional epitaxy.

Film degradation in air is a significant concern for growth of Bi₂Se₃. It has been shown to degrade in a variety of gases normally present in the atmosphere, leading to a
degradation of the topological surface states and an increase in carrier concentration. On the other hand, oxygen has been shown to act as a p-type dopant which reduces the bulk carrier concentration.
2.8 References

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Chapter 3
Experimental Procedure

3.1 Introduction

In order to fabricate Bi\textsubscript{2}Se\textsubscript{3} thin films, two methods were used: hybrid physical-chemical vapor deposition (HPCVD) and metal-organic chemical vapor deposition (MOCVD). This chapter will describe the experimental details related to these two growth methods, including substrate preparation, system design, growth parameters, and operating procedure. In addition, a study on the effects of different ambient environments on the electrical properties of Bi\textsubscript{2}Se\textsubscript{3} films over time was performed. Details of the experimental setup of and parameters of this study are also discussed. Finally, characterization techniques used to evaluate the thin films will be described.

3.2 Substrate Preparation

Several different materials were used as substrates for Bi\textsubscript{2}Se\textsubscript{3} growth. Sapphire (Al\textsubscript{2}O\textsubscript{3} (001)) was used for all growths unless otherwise noted. InP (111)B was used for several growths because of its very low lattice mismatch with Bi\textsubscript{2}Se\textsubscript{3} (0.24%). MgB\textsubscript{2} films grown on sapphire were used as substrates for bilayer experiments with the goal of producing proximity effect superconductivity in Bi\textsubscript{2}Se\textsubscript{3}. The sample preparation for each is described below.
3.2.1 Sapphire

Sapphire (001) was the substrate used for most growths in this study. While it has a relatively large lattice mismatch to Bi$_2$Se$_3$ (13.5%), this is not vitally important for van der Waals epitaxy. The ease of preparation, relative cost, and robustness made it the go-to substrate. It is also a rather inert surface, easing concerns of dangling bonds which inhibit type II growth of van der Waals epitaxy materials. It also has the advantage of being an insulator. This allows for significantly easier electrical measurements without having to account for transport through the substrate. Also, being an oxide itself, it does not degrade after longtime exposure to air.

(001) Sapphire was chosen because of it is a hexagonal-close-packed surface. A face of this arrangement has been shown to be important for well-oriented van der Waals epitaxy growth.$^1$

Sapphire (001) wafers were purchased from Cryscore Optoelectronic Limited. The 2” wafers were 99.996% pure with an Ra roughness of <0.2 nm. Surface preparation consisted of a 15 min ultrasonication clean in each of acetone and isopropanol followed by a de-ionized (DI) water dip and N$_2$ blow dry.

3.2.2 MgB$_2$

MgB$_2$ is a superconductor with $T_c = 39$K which has garnered interest for possible superconducting (SC) applications.$^2$ Of interest for this study is that a superconductor can, by the proximity effect, induce superconductivity in a topological insulator at a SC-TI interface.$^3$ This may give rise to Majorana fermions.
MgB$_2$ is a layered material with strong bonding within the layers.$^4$ The MgB$_2$-Bi$_2$Se$_3$ system may offer advantages over other SC-TI systems that have been used to study the proximity effect. The T$_c$ of MgB$_2$ is relatively high compared to materials used in previous studies.$^5$ Also, the layered nature of MgB$_2$ may allow easy growth of Bi$_2$Se$_3$. Above all, MgB$_2$ and Bi$_2$Se$_3$ can be grown in the same chamber without exposure to atmosphere. This can prevent the formation of an oxide barrier on the MgB$_2$ surface before growth of Bi$_2$Se$_3$.

Since Bi$_2$Se$_3$ was grown in situ immediately after MgB$_2$ growth, there was no substrate prep, per se, only cooling the substrate to the proper temperature for Bi$_2$Se$_3$ growth in an H$_2$ ambient environment.

### 3.2.3 InP (111)B

InP (111) has a near-ideal lattice mismatch to Bi$_2$Se$_3$ (0.24%). However, like Si, it forms a native oxide which must be removed in order to make use of this excellent lattice matching.

A two-step cleaning process has been used previously to create an oxide-free InP surface. A 2 minute etch in 4:1:100 H$_2$SO$_4$:H$_2$O$_2$:H$_2$O followed by a 30 second etch in 1:3 HCl:H$_2$O has been shown to leave a clean surface.$^6$ Heating the surface in a H$_2$ environment can then cause a H-terminated surface.$^7$

InP (111) wafers were purchased from axt. The 2” wafers were counter-doped with Fe to a resistivity of 5x10$^6$ Ω-cm.
InP substrates with several different preparation methods were utilized as described in section 4.4.2.

3.3 CVD Growth of Bi$_2$Se$_3$ Films

All growth of Bi$_2$Se$_3$ thin films were performed on a system originally designed for the HPCVD growth of MgB$_2$. The system was modified to accommodate the growth of Bi$_2$Se$_3$ by adding two metal-organic bubblers and the addition of a second heater to the system setup.

3.3.1 Growth Chamber

Deposition took place in a cold-walled vertical quartz chamber. A susceptor was held in place atop a quartz rod with a thermocouple inside to measure the susceptor temperature. The quartz growth chamber was water-cooled.

The susceptor was heated inductively using an Ameritherm, inc. power supply. A second resistive heater in conjunction with a thermocouple in a stainless steel shell was placed upstream of the susceptor. This setup can be seen in Figure 3-1.

The system vacuum was a rotary pump vacuum which could achieve a pressure of $5.5 \times 10^{-3}$ torr. The exhaust then traveled through a scrubber to neutralize any un-reacted gases. N$_2$ dilution was then used to dilute the exhaust, mostly H$_2$, below the lower explosive limit. The lines from the growth chamber to the pump would have to be
periodically cleaned due to excess selenium depositions. The pump oil was also changed periodically for the same reason.

Figure 3-1. Schematic of growth system with two heater setup

3.3.2 Safety

The metal-organic precursors used for growth (TMBi and DMSe) are pyrophoric materials, meaning that they combust on contact with air. DMSe and selenium pellets can produce \( \text{H}_2\text{Se} \) when in a hydrogen environment above 300°C.\(^8\) \( \text{H}_2\text{Se} \) is considered
the most toxic selenium compound\(^9\) and can attack the eyes and mucus membranes. Irritation becomes intolerable at 1.5 ppm.\(^{10}\) No human fatalities have been reported.

When a new MO source is installed, all connections are tightened and a He leak detector is hooked into the system. He gas is then sprayed around all connections in order to ensure that no leaks are present. The lines are then purged and pumped with H\(_2\) 10 times to ensure that all air has been purged from the lines before opening the metal-organic source. When a metal-organic source is removed, the line is purged and pumped 10 times with N\(_2\) to ensure that all of the metal-organic precursor has been removed from the line in order to prevent combustion when the line is opened to air.

All gas lines from the metal organic sources to the scrubber are contained within a well-ventilated enclosed chamber to prevent exposure even in case of a leak. This enclosure is equipped with air flow monitors that will alarm if the exhaust flow is too low.

In order to prevent H\(_2\)Se exposure to air, all exhaust from the system is run through a chemical scrubber.

The induction heater power supply is equipped with an emergency shut-off button in case of excessive heating. A single button can also close all pneumatic valves to shut off all gas flow in case of an emergency.
3.3.3 Operating Procedure

This section will discuss the experimental procedure for HPCVD and MOCVD. It will also detail the experimental method used for measuring the electrical measurements of samples over time in different ambient environments.

3.3.3.1 HPCVD

For Bi₂Se₃ growth using the HPCVD technique, the growth precursors were trimethyl bismuth (TMBI) and selenium pellets. The TMBI source was held in a stainless steel bubbler and was purchased from SAFC Hitech. The research grade bubbler was held at -10°C to control the TMBI vapor pressure according to the equation \( \ln(P_{\text{TMBI}}) = 7.628 - 1816/T(\text{K}) \). A pressure controller was used to hold the pressure inside the TMBI bubbler at 760 Torr.

The selenium source consisted of selenium pellets purchased from Alfa Aesar. The 99.999% pure, 2-6mm diameter pellets were placed in a ring around the substrate on the susceptor, shown in Figure 3-2. Five pellets, totaling approximately 0.25g, were normally used.

The susceptor was held in place by a quartz rod, which also contained a thermocouple to monitor the susceptor temperature.

After the sample was in place and the chamber sealed, the chamber was pumped down using a rotary pump to a pressure of \(~6 \times 10^{-3}\) Torr then purged with H₂ and pumped down again.
The chamber was then filled with H\textsubscript{2} to a pressure of, usually, 100 Torr with a small flow of H\textsubscript{2}, usually 30sccm. The top heater was then heated to the desired temperature, usually 350°C. When this temperature was reached, the susceptor was then heated to the desired temperature (220°C) at a rate of 50°C/min.

![Figure 3-2](image)

**Figure 3-2. (a)Schematic and (b) image of susceptor setup for HPCVD growth**

As the susceptor reached the desired temperature, a small H\textsubscript{2} flow, already flowing through a bypass valve, was switched to flow through the TMBi bubbler, usually 35 sccm. After the set growth time was elapsed, usually 10 min, the flow through the TMBi was switched back to the bypass. Both heaters were then turned off and the sample was allowed to cool in H\textsubscript{2}. When the chamber was cooled, it was pumped down and purged with N\textsubscript{2}. This was repeated a few times to evacuate any remaining un-reacted precursors. After the sample cooled to a temperature below 100°C, the chamber was opened and the sample was removed and stored in a N\textsubscript{2} box.

### 3.3.3.2 MOCVD

For MOCVD, the same TMBi source was used. Instead of the solid selenium pellets, however, another metal-organic source, dimethyl selenide (DMSe) was used as
the selenium source. The source was held at room temperature and the vapor pressure calculated from the equation \( \ln(P_{\text{DMSe}}) = 9.872 - 2224/T(\text{K}) \). A pressure controlled maintained the bubbler pressure at 760 torr. A mass flow controlled maintained the flow through the bubbler at typically 20-50 sccm. The operating procedure for MOCVD growth was much the same as for HPCVD. But, since an MO selenium source was used instead of selenium pellets, both precursors could be introduce once both heaters reached the desired temperatures, rather than selenium being slowly introduced as it heated up on the susceptor.

### 3.4 Characterization Techniques

Various characterization techniques were used to analyze the electrical and structural properties of Bi\(_2\)Se\(_3\) thin films. Each method is briefly discussed in this section.

#### 3.4.1 Hall Measurements

Hall measurements made using a custom-made system were performed in order to determine resistivity, carrier type, carrier concentration, and Hall mobility of the Bi\(_2\)Se\(_3\) films. After growth, samples were immediately brought to the Hall system and prepared in order to minimize contact with the air. Total time between taking the sample out of the growth chamber and the start of Hall measurements was 15-20 minutes. Indium dots were applied to the four corners of a sample and pressed into place in order to create an
ohmic contact. Ohmic contacts were confirmed using a curve tracer. Four point measurements were then performed to determine the resistivity of the film according to the equation: 
\[
\rho = \frac{\pi \times t}{\ln 2} \frac{R_{12,34} + R_{32,41}}{2} \times f,
\]
where t is the layer thickness, \( R_{12,34} \) and \( R_{32,41} \) are resistances measured through different contacts, and f is a correction factor based on the ratio of the resistances. Four point measurements were then performed in both a positive and negative magnetic field. The carrier type and density were then determined according to the equation 
\[
V_H = \frac{IB}{net}
\]
where \( V_H \) is the measured Hall voltage, I is the supplied current, B is the magnetic field strength, n is the carrier density, e is the charge of an electron, and t is the film thickness. Mobility is determined by the equation 
\[
\rho = \frac{1}{ne\mu}
\]
where \( \mu \) is the carrier mobility. Additional details on the Hall system used can be found in Dr. David Meyer’s thesis.

3.4.1.1 Hall Measurements over Time

In order to study the effect of different ambient environments on the electrical properties of Bi\(_2\)Se\(_3\) thin films, Hall measurements were performed on samples held in varying ambient environments.

This study seeks to understand how the electrical properties of Bi\(_2\)Se\(_3\) change over time in several different ambient environments in order to determine how each one affects the surface of Bi\(_2\)Se\(_3\). The first set of experiments done were a series of Hall measurements on several samples while they were held in different ambient environments, specifically air, nitrogen, water vapor in nitrogen, and oxygen. The
nitrogen was house nitrogen, boiled off from the building’s liquid nitrogen tank. The water vapor was introduced by flowing nitrogen through a DI water bubbler held at 40°C. The oxygen was 5N pure from a compressed cylinder. How the Hall measurements change over time in each of these environments can then be used to help understand how interaction with the ambient changes the film properties.

![Figure 3-3. Picture of Hall measurement system with plastic wrap to isolate from atmosphere in conjunction with flow of desired ambient gas.](image)

The sample was isolated from the surrounding environment and then exposed to a flow of the appropriate ambient gas of 1.5 slm. A simple plastic wrap was placed around the Hall measurement system in order to isolate the sample from the room environment (Figure 3-3). The flow of the desired gas was intended to keep contamination from the
outside environment to a minimum. Measurements were taken at set intervals of time (initially 10 min intervals, then 20 min, then up to several hours) and the resistivity, carrier concentration, and Hall mobility were plotted in order to show how the films reacted over time in each ambient environment.

3.4.2 X-ray Diffraction

X-ray diffraction was used to determine the phases present in the film and the film orientation and to assess the film quality. Initial glancing angle XRD to determine the phases present was done using a Rigaku DMAX Rapid II XRD system. It uses a Cu source and a curved image plate detector. Later to determine crystal quality and orientation, a Philips MRD four-circle diffractometer was used. It also used a Cu K\(_{\alpha1}\) radiation (\(\lambda=1.5406\text{Å}\)) source and a hybrid monochromator consisting of a parabolic-shaped multilayer x-ray mirror. Theta-2theta scans were performed to determine the planes perpendicular to the substrate and to ensure c-axis oriented growth. Rocking curve omega scans were performed to assess crystalline quality by determining the full width at half maximum (FWHM) of the (006) film peak. 360° phi scans were performed to determine if 6-fold rotation symmetry was present in the deposited films.
3.4.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed using both a Phillips XL-20 with a tungsten filament electron source and a LEO 1530 field-emission SEM (FESEM) which uses a Schottky field-emission electron source.

SEM was performed to analyze the film surface, making note of distinct features such as misaligned crystals and to determine film coverage. In some instances, cross-sectional imaging was used to determine film thickness.

3.4.4 Surface Profilometry

The thickness of the thin film samples was usually determined using stylus contact profilometry. In order to determine the thickness, a film was first scratched to reveal the bare substrate. Then, using a Tencor P-10 surface profilometer, a scan was taken across the scratched area. The height difference between the scratched area and the unscratched area was taken as the thickness.

3.4.5 Atomic Force Microscopy

AFM was used to more closely analyze the film surface by determining surface roughness and size and height of triagonal pyramids on the surface. This method was used when the concentration of misaligned crystals on the surface was low, otherwise the large differences in height would cause a streaky and unusable image. A Digital
Instruments Dimension 3100 Atomic Force Microscope was used for these measurements.

### 3.4.6 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface analysis technique that was used to monitor surface oxidation over time for films held in different ambient environments. For XPS measurements, a x-ray beam is focused on the sample surface. Photo-emitted electrons are then collected in a detector. The difference in energy between the incident x-rays and the emitted electrons is used to determine the types of bonding present on the surface. After growth, samples were as quickly as possible placed into the XPS vacuum chamber and pumped down to ensure minimal environmental contamination. If the samples were to be held in an ambient environment for a certain amount of time after growth, they were immediately transferred into this environment after growth. Then, after the specified amount of time, they were as quickly as possible transferred to the XPS chamber. A Kratos Analytical Axis Ultra was used for these measurements.

### 3.4.7 Transmission Electron Microscopy

The microstructure of the Bi$_2$Se$_3$ film was also investigated by cross-sectional transmission electron microscopy (TEM) using a JEOL 2010F field-emission microscope. This was used in order to determine the presence of stacking faults and other defects.
3.5 References

3 L. Fu and C. L. Kane, _Physical Review Letters_, **100** 096407 (2008)
11 L. J. van der Pauw, _Philips Technical Review_, **20** 220 (1958)
Chapter 4
Hybrid Physical-Chemical Growth of Bi$_2$Se$_3$ Thin Films

4.1 Introduction

As stated in the literature review (Ch. 2), one of the main factors leading to a high carrier concentration in Bi$_2$Se$_3$ thin films is selenium vacancies acting as donors. It has been shown that a high VI/V ratio can lead to decreased selenium vacancies, thus driving down the carrier concentration.\textsuperscript{1} This chapter focuses on growth of thin films of Bi$_2$Se$_3$ by HPCVD to minimize selenium vacancies by using a solid selenium source in close proximity to the growth substrate. The first set of growths involves the use of a single heated susceptor on which the substrate was placed and also the solid selenium source was held. This single heater was used to both decompose TMBi and evaporate the selenium source. The experimental equipment and technique was discussed further in Chapter 3. Because a single heater is used, it must be held at higher temperatures (300-400°C) than the melting point of the solid selenium source (220°C) in order to decompose TMBi. This causes constraints on the temperature range possible for growth. After it was determined that this technique could not be used to deposit single crystal Bi$_2$Se$_3$ films due to these constraints, a technique using a two heater setup was used to successfully deposit high quality single crystal films. The second part of this chapter describes the optimization of this two heater setup, discussed in section 3.3.1, one to promote decomposition of TMBi, the other to evaporate selenium. The effects that
changing the temperature of each of these heaters have on the electrical and structural properties of the Bi$_2$Se$_3$ films are the main focus of the second part of the chapter.

4.2 Single Heater HPCVD

4.2.1 Introduction

The first runs performed using the HPCVD process were done using a single heater to both decompose the TMBi and evaporate selenium. Since the selenium pellets are in a ring around the substrate, the substrate temperature is also the same as the selenium evaporation temperature. The first goal of these runs was to deposit a c-axis oriented Bi$_2$Se$_3$ film of the correct phase onto a sapphire substrate. The first set of runs was done in order to determine the temperature and pressure ranges in which this would be possible. A temperature range of 300-400°C and a pressure range of 10-600 Torr were studied. All growths were 5 minutes. The procedure for each run is described in chapter 3.

4.2.2 Growth Conditions

Unless otherwise noted, the growth conditions were as follows. The TMBi bubbler was held at 5°C and a pressure of 760 Torr with a flow of 50 sccm H$_2$ through the bubbler, resulting in a TMBi flow of 0.82 sccm. An additional 30 sccm H$_2$ was flown through the growth chamber, which was held at a pressure of 10-600 Torr. The susceptor
was held at temperatures from 300-400°C. Five pellets of selenium, or 0.25g were placed in the ring around the sapphire (001) substrate.

4.2.3 Temperature Study

Using a pressure of 100 Torr, samples were grown at 250°C, 300°C, and 400°C. Figure 4-1 shows a comparison of both SEM images and XRD scans of these three samples. The sample grown at 300°C has a much smoother surface with fewer droplets on the surface and only a relatively few misaligned crystals growing perpendicular to the surface. The XRD also shows that Bi_2Se_3 is the only phase present in growth. The (003) orientation is by far the dominant orientation, meaning that the c-axis of the film is mostly perpendicular to the surface. However, other orientations are also present, which is indicative of polycrystalline growth. The sample grown at 400°C, on the other hand, has a much rougher surface and has multiple phases present. The XRD shows that the Bi_3Se_4 and elemental Bi phases are present. This indicates a selenium deficiency during growth.

According to the Bi-Se phase diagram (Figure 4-2)^2, Bi_2Se_3 is the most Se-rich phase that this system will form. This means that above the melting point of selenium, Bi_2Se_3 will precipitate out as long as the supply of Se is sufficiently high. Since there is evidence of phases besides Bi_2Se_3 forming, this means that the selenium supply was insufficient to obtain the proper phase. The most likely cause of this is the Se supply running out during the growth. Since the selenium source consists of a finite amount of
Se pellets and not a constant gas source like for Bi, if the growth time is too long or the growth temperature is too high, the Se source will deplete, causing a Bi-rich environment.

Figure 4-1. SEM images and XRD theta-2theta scans of samples grown at (a and b) 250°C, (c and d) 300°C, and (e and f) 400°C.

Since the growth time is very short, only 5 minutes, it is most likely that the problem was too high of a growth temperature. Decreasing the temperature from 400°C to 300°C greatly alleviated this problem. Decreasing the temperature further would help keep the
selenium supply intact. The melting point of Se is 220°C and by visual inspection, the selenium pellets melted and nearly disappeared before the growth temperature was reached.

Figure 4-2. Phase diagram of Bi-Se binary system\(^2\)

However, while lowering the growth temperature further to 250°C does show film deposition, multiple orientations are still present (Figure 4-1b) and the additional problem arises that the entire film is covered in misoriented platelets (Figure 4-1a). This prevents using a substrate temperature in the range used most commonly in the MBE growth of Bi\(_2\)Se\(_3\) (200-250°C).\(^3,4\) As will be seen in the two heater growth section below, this increase in misoriented platelets is likely due to a very large VI/V ratio. As the temperature decreases, the Bi supply to the substrate decreases more quickly than the Se
supply to the substrate. Being able to control these two variables independently could allow greater flexibility in controlling the VI/V ratio and achieving single crystalline films with fewer misaligned platelets.

### 4.2.4 Pressure Study

Pressure can greatly affect growth during CVD. Increasing the pressure can promote decomposition of TMBi by increasing the residence time in the chamber by decreasing the gas velocity. This may help decompose TMBi at lower temperatures than may be possible at lower pressures. Increasing the pressure could also decrease the rapid evaporation of selenium by decreasing its partial pressure, allowing for longer growth times. However, increasing the chamber pressure can also lead to increased gas phase reactions. For this reason, understanding the effect of pressure on the HPCVD growth of Bi$_2$Se$_3$ is important. Using a temperature of 300°C, samples were grown at pressures of 10, 100, and 600 Torr. As can be seen in Figure 4-3a, at 10 Torr there is very little coverage with just small nucleation sites present on the substrate. At 100 Torr (Figure 4-3b), complete coverage is achieved with what appears to be overlapping flakes with a small number of misoriented crystals coming out of the surface. At 600 Torr (Figure 4-3c), the surface is completely covered in type I mis-aligned platelets. This may be due to either a faster growth rate preventing sufficient diffusion at the surface or from increased gas phase reactions leading to the nucleation of crystals of various orientations. Increasing the growth time at 10 Torr in order to promote greater film coverage was not possible due to the propensity of selenium to evaporate quickly, particularly at lower
pressures. Growth at 100 Torr seemed to give the best balance of growth rate and preventing gas phase reactions. 100 Torr was used in all subsequent growths.

Figure 4-3. SEM images of samples grown at (a) 50 Torr, (b) 100 Torr, and (c) 600 Torr
4.2.5 Single Heater Conclusions

While growth at 300°C and 100 Torr gave primarily c-axis oriented films of the correct phase, other orientations were also present. Other parameters, such as TMBi flow rate and starting the TMBi flow at the beginning of heating compared to starting it once the growth temperature was reached were also studied, but failed to have a significant impact on growth quality. Because of the temperatures required to decompose TMBi, growths had to be performed at temperatures above the substrate temperature range usually used for growth of Bi$_2$Se$_3$ by MBE. These higher temperatures also cause the solid selenium source to deplete quickly. Higher temperature may also cause the film growth to partially overcome the weak van der Waals bonding, which may have been the cause of even the best film, grown at 300°C, to have multiple grain orientations present. Lowering the growth temperature, in addition to lowering the partial pressure of selenium, also lowers the decomposition rate of TMBi. So, modifying the VI/V ratio is difficult while the decomposition of TMBi and the evaporation of selenium are both controlled by the susceptor temperature. It was determined that separating the TMBi decomposition temperature from the selenium evaporation temperature would be important for creating the proper conditions for high quality thin film growth.
4.3 Two Heater HPCVD

4.3.1 Introduction

After it was determined that growth with a single heater provided limited flexibility in being able to independently control the bismuth and selenium supplies, a second heater was installed upstream of the susceptor. The purpose of this second heater was to promote the decomposition of the TMBi source, for which a higher temperature is required, before it approaches the susceptor and substrate, which are held at a lower temperature. A higher temperature is required to help decompose TMBi. But, a lower temperature is necessary for the susceptor for two reasons. First of all, the solid selenium must be held at a lower temperature, otherwise it will evaporate too quickly above its melting point (220°C) and leave the Bi$_2$Se$_3$ film depleted of selenium. Secondly, a temperature in this range has been used for successful growth of c-axis oriented Bi$_2$Se$_3$ films$^5$ and higher temperatures may lead to more type I van der Waals growth with more misaligned crystals by partially overcoming the van der Waals bonding between the film and substrate. The modified chamber setup with the additional top heater is shown in Figure 4-4.
Figure 4-4. Schematic of growth chamber. Top thermal heater promotes cracking of TMBi and bottom heater heats substrate and elemental selenium source.

4.3.2 Growth Conditions

The main growth conditions that were studied were the temperature of both the top and bottom heaters. The top heater promotes the decomposition of TMBi while the bottom heater controls the evaporation of Se and is also the substrate temperature. Unless otherwise noted, the growth parameters were as follows. The TMBi bubbler was held at -10°C and a pressure of 760 Torr with a flow of 35 sccm H₂ through the bubbler, resulting in a TMBi flow of 0.245 sccm. An additional 65 sccm H₂ was flown through the growth chamber, which was held at a pressure of 100 Torr. The top thermal heater was held at temperatures from 290-540°C and the bottom heater was held at temperatures
from 160-260°C. Five pellets of selenium, or 0.25g were placed in the ring around the sapphire (001) substrate.

**4.3.3 Experimental Procedure and Results**

The procedure outlined in section 3.4.1 was used for all two-heater HPCVD growths. The first set of experiments involved varying the top heater temperature from 290-540°C while holding the bottom heater at 220°C to determine its effects on growth rate, electrical properties and structural properties. The second set of experiments involved varying the bottom heater temperature from 160-260°C while holding the top heater at 350°C in order to determine its effects on the electrical and structural properties of the thin films.

**4.3.4 Top Heater Study**

**4.3.4.1 Growth Rate**

Varying the temperature of the top, upstream heater had a significant impact on the growth of Bi$_2$Se$_3$ thin films. The first difference noted is a direct relationship between the top heater temperature and the film growth rate. The growth rate increases steadily with increasing top heater temperature from 1.9 nm/min at 290°C to 5.2 nm/min at 500°C, before decreasing at 540°C to 4.5 nm/min. This increase is likely due to an increased percentage of the TMBi decomposing as it passes the top heater as the temperature increases. However, at 540°C the temperature may increase so much that it
causes more bismuth to deposit on the chamber side walls before it reaches the substrate, leading to a decrease in the growth rate. This trend can be seen in Figure 4-5a.

If the growth rate is limited by the decomposition rate of TMBi, the growth rate should follow an Arrhenius trend, specifically \( \text{growth rate} \propto e^{-\frac{E_a}{RT}} \), where \( E_a \) is the activation energy of the decomposition reaction, \( R \) is the universal gas constant, and \( T \) is the temperature in Kelvin. Excluding the growth at 540°C, the rest of the data was plotted as the natural log of growth rate versus inverse temperature in order to determine Arrhenius dependence. The slope of this plot is \( -\frac{E_a}{R} \). Multiplying the slope by the gas constant, \( R \), should then give the activation energy of the growth rate. As can be seen in Figure 4-51b, the data fits to this trend reasonable well. However, the slope gives an activation energy of 17.17 kJ/mol, significantly lower than the reported activation energy for the decomposition of TMBi, 141 kJ/mol. Also, the data doesn’t completely fit a line in this plot. This suggests that the growth rate is not limited by TMBi decomposition.

There are two other phenomena that may be considered to explain the dependence of growth rate on temperature. Earlier reports of MOCVD growth of Bi\(_2\)Se\(_3\) showed a decrease in growth rate at higher VI/V ratios, keeping all else constant. Since lowering the temperature of the top heater presumably also decreases the amount of Bi available at the substrate for reaction, then decreasing the top heater temperature also effectively decreases the VI/V ratio (this will be discussed in greater detail below). So, in addition to the temperature dependence, the growth rate may also be affected by an increasing VI/V ratio at lower temperatures.
Figure 4-5. Effect of top heater temperature on growth rate (a) growth rate versus top heater temperature with power law fit, and (b) natural log of growth rate versus inverse top heater temperature with Arrhenius fit.
The other possible cause for the activation energy being significantly lower than the TMBi decomposition activation energy may be that the growth rate is not TMBi decomposition-controlled and may be in a mass transport-controlled growth region for the range of temperatures studied. Diffusion-limited growth follows a power law dependence on temperature from the equation \( D = D_0 \left( \frac{T}{T_0} \right)^n \frac{P_0}{P} \), where \( D \) is the gas phase diffusion coefficient, \( D_0, T_0, \) and \( P_0 \) are the reference diffusion coefficient, temperature and pressure, and \( n \) is an experimentally determined exponent (usually 1.5-2). As seen in Figure 4-5a, the growth rate versus temperature data for the temperature range 290-500°C fits well to a power law dependence, with \( R^2 = 0.973 \) and an exponent of 1.81, within the range of 1.5-2 usually seen for diffusion-controlled growth. While both the Arrhenius function and the power law-controlled diffusion equation fit the data well, the experimentally-determined exponent (\( n=1.81 \)) conforms to the expected value much more than the experimentally-determined activation energy. Thus it is likely that the growth rate has a diffusion-controlled dependence on the top heater temperature. As will be shown later, the bottom heater temperature also affects the growth rate.

4.3.4.2 Structural Properties

4.3.4.2.1 Surface Morphology

The top heater temperature also had an effect on the structural properties of Bi\(_2\)Se\(_3\) films. Figure 4-6 shows the surface of samples grown at 290°C, 390°C, and 500°C. There are several significant differences seen in the samples grown at different
temperatures. The first of these is the size of the pyramidal-shaped structures on the surface.

Figure 4-6. Growth of Bi$_2$Se$_3$ while varying top heater temperature: (a) 290°C, (b) 390°C, and (c) 540°C
The surface of Bi$_2$Se$_3$ is made up mostly of triagonal pyramid structures. According to Lui, et al. these pyramids are caused when a growing layer encounters an obstacle or another growth layer and becomes pinned. The layer is able to grow over the obstacle, but the growth direction is changed. As this process repeats itself, a triagonal pyramid is formed from a spiral growth mode. This is seen in Figure 2-5a in the Literature Review.

![AFM images](image)

**Figure 4-7.** AFM of samples grown with a top heater temperature of (a) 290°C (RMS roughness = 5.1 nm) and (b) 500°C (RMS roughness = 1.28 nm)
Changing the top heater temperature showed a significant impact on the size and density of these pyramids. As can be seen in the AFM images in Figure 4-7, the pyramids on a sample grown at 290°C (edge length average of 820 nm) appear much larger both in width and height compared to a sample grown at 500°C (edge length average of 380 nm). Ignoring the white spots caused by misoriented crystals on the surface, which are out of the scale range, the sample with a top heater T of 290°C has much larger pyramids with many more step edges visible than the sample grown at 500°C. This is quantified by the RMS roughness, with the sample grown at 290°C having a roughness of 5.1 nm compared to 1.2 nm for the sample grown at 500°C.

![Figure 4-8. Roughness versus growth rate for films grown with varying top heater temperature](image)
The difference in the triagonal feature size is likely due to differences in the growth rate. If the film grows more slowly from fewer nucleation sites, the initial islands will extend farther before they encounter each other and start to spiral due to pinning. This is demonstrated in Figure 4-8, which shows a direct correlation between growth rate and surface roughness. Misaligned crystals were excluded from the roughness calculations in order to more accurately measure the pyramid roughness. At lower growth rate, the grain size is larger grains but the overall surface roughness is increased.

The second difference seen on the surface with varying temperature is the presence of misaligned crystals on the film surface. Films at both ends of the temperature range have higher misaligned platelet densities than films in the middle of the range. This is shown quantitatively in Figure 4-9, which plots platelet density versus top heater temperature. An increase in misaligned crystals (type I growth) has been previously attributed to many factors for 2D layered growth, particularly oxygen incorporation, growth temperature, source partial pressure, and film growth rate.

The platelet density increases steadily above 400°C, while the growth rate is also increasing. As the growth rate increases, it may allow for less time for nucleation sites to grow in the c-axis-oriented direction, leading to more misaligned growth. This, however, does not explain the increase in platelet density on the low end of the temperature range. Bayaz, et al. saw a decrease in crystal quality at greater VI/V ratios. And so, as the top heater temperature decreases and the effective VI/V ratio increases, the crystal quality may be decreasing as evidenced by an increased density of misaligned crystals on the
As the effective VI/V ratio becomes very large, excess selenium may act as nucleation sites for other orientations at the surface.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{platelet_density_vs_top_heater_temperature.png}
\caption{Platelet density versus top heater temperature}
\end{figure}

4.3.4.2.2 X-ray Diffraction

X-ray diffraction data across the whole range of top heater temperatures studied showed strongly c-axis oriented films. Shown in Figure 4-10, the sample grown at 500°C gives representative data for the entire growth range. In a theta-2theta scan, only peaks from the (003) family of peaks are seen. This is evidence of a strongly c-axis oriented film. Also seen in Figure 4-10b is a phi scan of the off-axis (015) peak. The 6 peaks in
this can indicate 6-fold symmetry, meaning that the film is well-oriented rotationally within the plane of the substrate in addition to the c-axis being perpendicular to the substrate surface. This is also seen through the entire top heater temperature range.

![Graph](image)

**Figure 4-10.** Typical XRD data for two-heater HPCVD-grown film, (a) theta-2theta and (b) 360 phi scan of (015) peaks

As seen in Figure 4-11, the rocking curve FWHM of the (006) peak remains constant throughout the temperature range studied, remaining at about 0.046°. However, the shape of the rocking curve peak does change slightly over the temperature range studied. While the peaks for films grown at 350°C and 500°C are symmetrical, the peak for a film grown at 290°C is decidedly asymmetrical with a shoulder on the higher angle
An asymmetrical rocking curve has previously been attributed to a damaged surface layer with residual stress in GaN films.\textsuperscript{14} Taking into account the varying growth rates, samples were grown for different times depending on the growth rate in order to ensure similar thicknesses for all films. In other words, a sample grown at 290°C was grown for 11.5 minutes, while the sample grown at 500°C was only grown for 5 minutes.

![Figure 4-11. Rocking curve of the (006) peak for samples grown at 290°C (FWHM = 0.0475°, red), 350°C (FWHM = 0.0441°, blue), and 500°C (FWHM = 0.0463°, green).](image)

This means that the longer a sample was grown for, the higher the rocking curve omega angle tends to be. Prominently, within the sample grown at 290°C, there is even a shoulder that tends to an even higher angle. It is possible that the cause of this is a
varying supply of selenium over time. As the selenium supply depletes after higher growth times, this may lead to a slight change in the d-spacing. So, a sample with a smaller selenium supply after a long growth time may have a lower d-spacing due to selenium vacancies. The shoulder in the sample grown at 290°C may be due to this depleting selenium supply even within a single growth run.

4.3.4.3 Electrical Properties

The most relevant effect that the top heater temperature has is that on the electrical properties of \( \text{Bi}_2\text{Se}_3 \). Figure 4-12 shows the Hall mobility and carrier concentration for films grown with a top heater temperature from 290-540°C. From 320-540°C, there is a clear trend for higher carrier concentration and lower mobility, with the carrier concentration increasing from \( n=9.16 \times 10^{18} \text{ cm}^{-3} \) at 320°C to \( n=1.47 \times 10^{19} \text{ cm}^{-3} \) at 540°C and mobility decreasing from \( \mu=715 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) to \( \mu=552 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) over the same range. As seen in Figure 4-12, this is a rather steady increase in the carrier concentration over this range, but not a very large increase overall. The increase in carrier concentration can be explained by the higher top heater temperatures promoting decomposition of TMBi, thus lowering the VI/V ratio and increasing the selenium vacancy concentration. Since selenium vacancies act as double donors, this would increase the n-type carrier concentration, which is what is seen.
Table 4-1. Top Heater Temperature Effects Summary

<table>
<thead>
<tr>
<th>Top Heater Temperature (°C)</th>
<th>Growth Time (min)</th>
<th>Film Thickness (μm)</th>
<th>Growth Rate (nm/min)</th>
<th>Carrier concentration (cm⁻²)</th>
<th>Hall Mobility (cm²/V·s⁻¹)</th>
<th>(006) FWHM (°)</th>
<th>Surface Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>11.5</td>
<td>21.7</td>
<td>1.89</td>
<td>1.63x10¹⁹</td>
<td>569</td>
<td>0.0475°</td>
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<td>2.58</td>
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<td>3.00</td>
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<td></td>
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<td></td>
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<td>27.1</td>
<td>4.33</td>
<td>9.94x10¹⁴</td>
<td>641</td>
<td></td>
<td>1.6</td>
</tr>
<tr>
<td>470</td>
<td>5.6</td>
<td>27.4</td>
<td>4.90</td>
<td>9.71x10¹⁴</td>
<td>626</td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>500</td>
<td>5.0</td>
<td>26.1</td>
<td>5.22</td>
<td>1.24x10¹⁹</td>
<td>564</td>
<td>0.0463°</td>
<td>1.3</td>
</tr>
<tr>
<td>540</td>
<td>6.36</td>
<td>28.4</td>
<td>4.47</td>
<td>1.47x10¹⁹</td>
<td>552</td>
<td></td>
<td>1.8</td>
</tr>
</tbody>
</table>

The decrease in mobility that accompanies this is related. The higher the carrier concentration is, the higher the vacancy concentration, leading to greater ionized impurity scattering. This then decreases the mobility. Since the XRD is nearly identical for the entire temperature range, it is likely that selenium vacancies are the primary cause of the change in carrier concentration and mobility over the top heater temperature range.

However, at 290°C, the lowest temperature studied, there is a sudden shift in this trend, with the carrier concentration shooting up to 1.67x10¹⁹ cm⁻³ and mobility decreasing to 509 cm²V⁻¹s⁻¹. This may be caused by the increasing VI/V ratio eventually leading to Se₆Bi antisite defects. Se₆Bi defects are donors and predicted to occur in an overly selenium-rich environment.
4.3.5 Bottom Heater Study

4.3.5.1 Growth rate

The next study was to vary the bottom heater temperature from 160°C to 260°C while keeping the top heater constant at 350°C. All other parameters were held constant as described above. For growths at 160°C and 180°C, there was no deposition on the substrate. This is likely because the selenium vapor pressure was insufficient to act as a supply for notable film growth. No Hall measurements could be taken as no film was
deposited. Significant growth did not begin until 200°C. The growth rate increased slightly from 1.8 nm/min at 200°C to 2.1 nm/min at 220°C. It then increases more significantly above this temperature, nearly tripling to 6.1 nm/min at 260°C (Figure 4-13). This inflection point is likely related to the melting point of selenium, 221°C. Above this temperature, the growth rate is much more dependent on temperature since the source is then a liquid. The four films from 220-280°C show a linear trend with $R^2=0.989$ when the log of growth rate is plotted against inverse temperature. The vapor pressure dependence on temperature generally follows the form $\log P = B - A/T$, where $A$ and $B$ are experimentally determined coefficients for each material. Our experimental data gives the $A$ coefficient, the slope as 3701 whereas the value accepted from the literature is 4722. There are then likely other factors that impact the growth rate besides the selenium evaporation temperature alone. Since the selenium evaporation temperature and the substrate temperature are the same, the increased substrate temperature may shift the adsorption equilibrium and partially counteract the effect of the increased selenium partial pressure. The growth rate is dependent on both the supply of bismuth and selenium available at the surface. The growth at 200°C does not fit the trend of the other growths. But, as will be seen when discussing the structural properties of these films below, the 200°C growth was a special case, likely due to the selenium source still being a solid at this point.
4.3.5.2 Structural Properties

4.3.5.2.1 Surface

Figure 4-14 shows SEM images of samples grown at 200°C, 220°C, and 260°C. The samples grown at 220°C and 260°C show similar structures, large triagonal pyramids with misaligned platelets on the surface, though the sample grown at 260°C seems to have a larger concentration of these platelets. This could be due to either a higher growth rate at higher temperatures or the higher substrate temperature allowing growth to partially overcome the weak van der Waals bonding, leading to more type I growth. The sample grown at 240°C also shows similar structures. However, the sample grown at
200°C shows a significantly different structure. Instead of large triangular features, the film appears to have a much more granular structure with small grains covering the surface. As will be seen, this has a significant impact on the XRD and electrical properties of this film.

Figure 4-14. SEM images for samples grown at (a and b) 200°C, (c and d) 220°C, and (e and f) 260°C.
4.3.5.2.2 X-Ray Diffraction

X-ray for all the films of this study showed only the (003) family of peaks in theta-2theta scans, an example of which is shown above in Figure 4-10. For samples grown at 220° and above, the x-ray data conforms to that described above for the top heater study. This means that the (006) rocking curves had a very small FWHM (0.0511° at 260°C) and the phi scan of the (015) peak showed 6-fold symmetry. The sample grown at 200°C, however, was much different. As can be seen in Figure 4-15, the rocking curve of the sample grown at 200°C shows a much broader and weaker rocking curve peak than the samples grown at higher temperatures. This shows that this sample is not nearly as c-axis oriented as the other films in the series. It also does not exhibit the 6-fold symmetry of the (015) peak like the other films. Therefore, it is not a single crystal film.

At the other end of the lower heater temperature range studied, the film grown at 280°C showed poor structural quality compared to the other samples. As seen in Figure 4-16, other orientations besides the (003) family of peaks are present in a theta-2theta scan. The film is clearly polycrystalline. This is also evident in an SEM image of the surface seen in Figure 4-17a. There are several possible reasons for the very large increase in misaligned platelets formed and other orientations present at 280°C compared to lower temperature samples. The first possibility is that the growth rate increased to such an extent that the precursors have insufficient time to diffuse at the surface, leading to the growth of grains of varying orientations rather than the preferred orientation with the c-axis perpendicular to the substrate surface.
Figure 4-15. Rocking curve of the (006) peak for samples grown at 200°C (FWHM = 0.1022°, red), 220°C (FWHM = 0.0422°, blue), 260°C (FWHM = 0.0511°, green), and 280°C (FWHM = 0.0347°, purple).

In order to investigate this, a second growth was performed with the lower heater at 280°C, but the flow rate through the TMBi bubbler was cut in half, cutting the growth rate in half. Cross sectional SEM was used to confirm that there is a c-axis oriented film in addition to the large density of misaligned platelets covering the surface (Figure 4-17c). This agrees with the XRD 2-theta scan seen in Figure 4-16, which shows strong intensities from the (003) c-axis oriented family of reflections. This underlying planar film is likely responsibly for electrical transport since the electrical properties don’t vary significantly from samples with much lower platelet densities (section 4.3.5.3). Film thicknesses and growth rates for these samples were also confirmed using cross sectional SEM since the large misaligned platelet density made measurements by the usual profilometry technique difficult. As can be seen in Figure 4-17, the surface of a sample growth with this lower growth (7.7 nm min⁻¹) rate had a surface similar to the sample grown...
with a higher growth rate (14.2 nm min⁻¹) with misaligned platelets covering the entire surface. Therefore, the growth rate alone is not the cause of the polycrystalline growth. The other possibilities which cause this polycrystalline growth involve the substrate temperature and the Se partial pressure. The higher substrate temperature may be high enough to partially overcome the weak van der Waals bonds responsible for the van der Waals epitaxy growth of Bi₂Se₃, leading to other orientations more easily growing. Another possibility is that the higher Se partial pressure at 280°C causes increased vapor phase reactions and precipitates depositing on the surface may act as catalyst for other crystallographic orientations than the preferred c-axis orientation.

Figure 4-16. Theta-2theta scan of film grown with bottom heater temperature of 280°C, clearly showing multiple orientations present.
Figure 4-17. Films grown at 280°C lower heater temperature with (a) normal growth rate (14.2 nm min$^{-1}$), (b) reduced growth rate (7.7 nm min$^{-1}$), (c) cross sectional image of film grown at 280°C, and (d) lower magnification cross sectional image of the same film.

4.3.5.3 Electrical Properties

The bottom heater temperature also had a significant impact on the electrical properties of the films. As can be seen in Figure 4-18, the carrier concentration decreases with increasing bottom heater temperature while mobility increases over this same range. Carrier concentration decreases significantly from 3.73x10$^{19}$ cm$^{-3}$ at 200°C to 7.28x10$^{18}$ cm$^{-3}$ at 260°C and decreasing even further to 6.5x10$^{18}$ cm$^{-3}$ at 280°C. This overall trend is likely due to an increase in the VI/V ratio, and thus a decrease in selenium vacancies due to higher selenium vapor pressure at higher bottom heater temperatures.
The mobility also increased significantly over the same range, from 28 cm²V⁻¹s⁻¹ at 200°C to 697 cm²V⁻¹s⁻¹ at 240°C before dipping slightly to 668 cm²V⁻¹s⁻¹ at 260°C and dropping even farther to 599 cm²V⁻¹s⁻¹ at 280°C. The very large jump between 200°C and 220°C is likely related to the change in structure seen in the previous section for the sample grown at 200°C. The drop in mobility above 240°C is likely due to the increased platelet density at 260°C and even multiple orientations present in the sample grown at 280°C. This overall trend is likely due to an increase in the VI/V ratio, and thus a decrease in selenium vacancies due to higher selenium vapor pressure at higher bottom

<table>
<thead>
<tr>
<th>BottomHeater Temperature (°C)</th>
<th>Growth Time (min)</th>
<th>Film Thickness (μm)</th>
<th>Growth Rate (μm/min)</th>
<th>Carrier concentration (cm⁻³)</th>
<th>Hall Mobility (cm²V⁻¹s⁻¹)</th>
<th>(006) FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>10</td>
<td>18.6</td>
<td>1.86</td>
<td>3.72×10¹⁹</td>
<td>28</td>
<td>0.1022</td>
</tr>
<tr>
<td>220</td>
<td>10</td>
<td>20.7</td>
<td>2.07</td>
<td>1.41×10¹⁹</td>
<td>525</td>
<td>0.0422</td>
</tr>
<tr>
<td>240</td>
<td>10</td>
<td>36.6</td>
<td>3.66</td>
<td>8.10×10¹³</td>
<td>697</td>
<td></td>
</tr>
<tr>
<td>260</td>
<td>10</td>
<td>60.9</td>
<td>6.09</td>
<td>7.29×10¹¹</td>
<td>668</td>
<td>0.0511</td>
</tr>
<tr>
<td>280</td>
<td>10</td>
<td>142</td>
<td>14.2</td>
<td>6.5×10¹⁸</td>
<td>599</td>
<td>0.0347</td>
</tr>
</tbody>
</table>
heater temperatures.

Figure 4-18. Mobility and carrier concentration versus bottom heater temperature

4.3.6 Low Temperature Transport Measurements

4.3.6.1 Temperature Dependent Hall

Since most electrical measurements in the literature are done at low temperatures, one sample was chosen on which to perform low temperature Hall and magneto-resistance measurements. This particular sample was grown with a top heater temperature of 375°C and a lower heater temperature of 220°C. All other parameters were as reported above in section 4.2.2.
This particular sample had a room temperature carrier concentration of $1.0 \times 10^{19}$ cm$^{-3}$ and a mobility of $671 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and was approximately 30 nm thick. First, the sample was patterned according to the diagram in Figure 4-19 by contact lithography and lift off to enable more precise measurements.

Figure 4-19. Pattern used for low temperature Hall and magnetoresistance measurements.

Then, Hall measurements were taken at temperatures from 300K down to 2.4K. The results are shown in Figure 4-20. The carrier concentration remained nearly constant throughout the temperature range at about $1.1 \times 10^{19}$ cm$^{-3}$. The mobility, however, increases significantly from $799 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at room temperature to $1700 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 2.4K. The difference in the room temperature mobility measurements is likely due to better contacts and a smaller area being measured in the carrier concentration versus temperature measurements. The resistivity behavior is related to the mobility behavior. As the mobility increases then levels out below 40K, the resistivity decreases from a value of $7.54 \times 10^{-4} \Omega \text{-cm}$ then levels out below 40K at $3.4 \times 10^{-4} \Omega \text{-cm}$. This is similar to previously-reported data for MBE growth on Si$^{18}$ and is indicative of metallic behavior. Mobility increases as thermal lattice vibrations decrease with decreasing temperature. At
some point, in this case about 40K, thermal vibrations cease to be the dominant factor and lattice defects become dominant. This causes the resistivity to remain constant with regard to temperature below this temperature. This metallic behavior indicates that the Fermi energy is in the conduction band for the entire temperature range studied.

Figure 4-20. (a) resistivity and (b) mobility and carrier concentration versus measurement temperature for two-heater grown film.
4.3.6.2 Magneto-resistance Measurements

The resistance of Bi$_2$Se$_3$ with respect to magnetic field shows a power law dependence, but with an anomalous drop around zero field, which is caused by weak antilocalization.$^{19}$ Weak antilocalization is a result of strong spin-orbit coupling affecting carrier diffusion$^{20}$ can be a signature of topological insulator surface states$^{21}$ or simply an effect of bulk strong spin-orbit coupling.$^{22}$ At low temperatures, a dip in resistivity versus magnetic field around zero field is indicative of weak antilocalization, and thus indicative of TI surface states. For magneto-resistance measurements done at 4.2K, this dip is clearly visible, as seen in Figure 4-21.

![Magneto-resistance data for sample held at 4.2K](image)

Figure 4-21. Magneto-resistance data for sample held at 4.2K. Insert shows low field detail.
4.4 Addition Structural Studies

4.4.1 Transmission Electron Microscopy

Cross-sectional transmission electron microscopy (TEM) was performed on a Bi$_2$Se$_3$ film grown with the two-heater method. This particular sample was grown with a top heater temperature of 375°C and a lower heater temperature of 220°C. All other parameters were as reported above in section 4.2.2. Figure 4-22a is a low-magnification bright-field TEM image of the Bi$_2$Se$_3$ film, collected along the [100] zone axis under multi-beam diffraction conditions. The Bi$_2$Se$_3$ was originally attached to the sapphire but delaminated from the substrate during sample preparation. Electron diffraction confirmed the epitaxial growth of the film. However, the film was found to consist of a high density of planar defects, which caused the diffraction contrast variation in the image. Figure 4-22b is a high-resolution TEM (HR-TEM) image of the film, which reveals that the film consists of subgrains separated by planar defects such as stacking faults and twin boundaries. The twin boundaries revealed in the HRTEM image are consistent with the presence of oppositely oriented triangular features as discussed in section 2.3.3.
Figure 4-22. (a) Low-magnification bright-field and (b) high-resolution TEM images of the Bi$_2$Se$_3$ film. The sapphire substrate is not in the viewing area since the film had delaminated from it. The arrows in (b) indicate two twin boundaries lying on the (001) plane.

4.4.2 Substrate Comparison

A comparison was done between films grown with the same conditions on the normally-utilized substrate, sapphire (001), and InP (111)B. InP (111)B is of interest because it is nearly lattice matched to Bi$_2$Se$_3$ (0.24% mismatch). Unlike Al$_2$O$_3$, the surface of InP must be etched before growth to remove a native oxide. InP substrates prepared by three different methods were used for Bi$_2$Se$_3$ growth alongside a normally-prepared Al$_2$O$_3$ substrate. All samples were cleaned with the normal acetone and IPA sonication described in section 3.2.1. One InP was then grown as-is. Another sample was placed in nanostrip for 60 min. Another InP sample was placed in nanostrip for 60
min then 20% HCl for 2 min. These conditions are summarized in Table 4-3. The four substrates (1 sapphire and 3 InP) were then placed into the growth chamber and Bi$_2$Se$_3$ was deposited using conditions summarized in Table 4-4.

**Table 4-3. Properties of Films Grown on Different Substrates**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Al$_2$O$_3$ – Acetone and IPA</th>
<th>InP – 60 min nanostrip</th>
<th>InP – 60 min nanostrip + 2 min 20% HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(006) FWHM (°)</td>
<td>0.0444</td>
<td>1.1562</td>
<td>0.3281</td>
</tr>
<tr>
<td>(015) FWHM (°)</td>
<td>4.6</td>
<td>0.7670</td>
<td>0.2478</td>
</tr>
<tr>
<td>Carrier Concentration (cm$^3$)</td>
<td>1.6x10$^{19}$</td>
<td>1.5x10$^{19}$</td>
<td>8.6x10$^{19}$</td>
</tr>
<tr>
<td>Mobility (cm$^2$V$^{-1}$s$^{-1}$)</td>
<td>612</td>
<td>383</td>
<td>416</td>
</tr>
<tr>
<td>Film Thickness (nm)</td>
<td>33.1</td>
<td>31.7</td>
<td>30.7</td>
</tr>
</tbody>
</table>

SEM, XRD, and Hall measurements were then performed on each sample. The SEM images for each sample can be seen in Figure 4-23. The sample grown on sapphire shows triangular pyramids with some misaligned platelets as usually seen (Figure 4-23a).

**Table 4-4. Growth Conditions for Films Grown on Different Substrates**

<table>
<thead>
<tr>
<th>Bottom Heater Temperature</th>
<th>240°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Heater Temperature</td>
<td>350°C</td>
</tr>
<tr>
<td>Growth Time</td>
<td>10 min</td>
</tr>
<tr>
<td>Pressure</td>
<td>100 Torr</td>
</tr>
<tr>
<td>TMBt Flow rate</td>
<td>0.245 sccm</td>
</tr>
</tbody>
</table>

The sample grown on un-etched InP (Figure 4-23b) is completely covered in misaligned platelets. The sample grown on InP which had been placed in nanostrip for 60 min
(Figure 4-23c) shows a very smooth surface with a reduced density of misaligned platelets. The sample grown on InP which had been placed in nanostrip for 60 min and HCl for 2 min (Figure 4-23d) also shows a very smooth surface with small triangular pyramids and a very low density of misaligned platelets.

XRD measurements were performed on the samples grown on sapphire, InP etched in nanostrip, and InP etched in nanostrip and HCl. The sample grown on sapphire has rocking curves similar to what was observed previously. The (006) rocking curve FWHM is 0.0444° (Figure 4-24a) and the off axis (015) rocking curve is much broader, FWHM = 4.6° (Figure 4-24b). The samples grown on InP have broader peaks for the (006) reflection and sharper peaks for the (015) reflection. The sample grown on InP
etched in only nanostrip had a (006) FWHM = 1.1562° (Figure 4-24c) and a (015) FWHM = 0.7670° (Figure 4-24d). The sample grown on InP etched in nanostrip and HCl had a (006) FWHM = 0.3281° (Figure 4-24e) and a (015) FWHM = 0.2478° (Figure 4-24f). This increase in the FWHM for the (006) peak rocking curve seen for both samples grown on InP means that there is increased tilt in the Bi$_2$Se$_3$ subgrains with respect to the substrate compared to samples grown on sapphire.

4-24. Samples grown on sapphire (a) (006) (FWHM = 0.0444°) and (b) (015) (FWHM = 4.6), InP etched in nanostrip for 60 min (c) (006) (FWHM = 1.1562°) and (d) (015) (FWHM = 0.7670°), and InP etched in nanostrip for 60 min and HCl for 2 min (e) (006) (FWHM = 0.3281°) and (f) (015) (FWHM = 0.2478°).
This may be because the etching leaves a rougher surface or because of dangling bonds on the InP surface left by etching. The decrease in the FWHM for the off axis (015) peak means that there is less twist between subgrains for the samples grown on InP. They are more well-aligned, likely because of the better lattice mismatch between InP (111) and Bi$_2$Se$_3$. Therefore, the first Bi$_2$Se$_3$ layer is more likely to be well-aligned to the substrate.

Hall Measurements performed on these samples show little change in the carrier concentration between substrates and etching conditions. The carrier concentration remained at 1.5-1.6x10$^{19}$ cm$^{-3}$ for the samples grown on sapphire, InP etched in nanostrip, and InP etched in nanostrip and HCl. The mobility, however, decreased for the samples grown on InP compared to sapphire. While the mobility for a film grown on sapphire was 612 cm$^2$ V$^{-1}$s$^{-1}$, the mobilities for the samples grown InP etched in nanostrip and on InP etched in nanostrip and HCl were 383 cm$^2$ V$^{-1}$s$^{-1}$ and 416 cm$^2$ V$^{-1}$s$^{-1}$ respectively. This drop in mobility for samples grown on InP compared to sapphire is likely related to the increased tilt evident from the (006) rocking curves. The smaller grains size seen in SEM of the samples grown on InP would also lead to an increased number of grain boundaries and possible more twist between these grains. This increased tilt may mean an increased density of twin boundaries and other scattering sites. While the HCl etch should leave the surface H-terminated, other passivation methods may need to be studied including prolonged exposure to Se before growth begins.
4.5 Summary

Controlling the evaporation temperature for the solid selenium source and the decomposition temperature for the bismuth source are very important factors for achieving epitaxial thin films of Bi$_2$Se$_3$. Using a single heater to both evaporate selenium and decompose TMBi met with limited success. A temperature range from 250-400°C was used. At 400°C, the selenium evaporated too quickly to act as a reliable supply for film growth and Se-deficient phases such as Bi$_3$Se$_4$ were deposited. Dropping the growth temperature to 300°C resulted in the deposition of the proper phase, Bi$_2$Se$_3$. And, while the film was mostly c-axis oriented, multiple orientations were still present. Dropping the temperature further down to 250°C resulted still in multiple orientations being deposited in addition to a high concentration or randomly-oriented platelets on the film surface. It was thought that this is due to an overly large VI/V ratio due to the Bi supply decreasing more rapidly than the Se supply when growing at lower temperatures. It was determined that being able to independently control the Se and Bi supplies would greatly aid in the growth of epitaxial thin films of Bi$_2$Se$_3$.

A second heater was installed upstream of the susceptor with the intention of promoting the decomposition of TMBi before reaching the substrate independently of the susceptor temperature used to evaporate selenium. Two sets of runs were performed. One varied the top heater temperature while keeping the bottom heater temperature constant at 220°C. The other varied the bottom heater temperature while keeping the top heater constant at 350°C. For the entire top heater temperature range studied, completely
c-axis oriented films were deposited exhibiting 6-fold symmetry indicative of epitaxial growth.

Decreasing the top heater temperature increased the effective VI/V ratio, leading to an decreased carrier concentration for most of the temperature range studied (1.47x10^{19} \text{ cm}^{-3} at 540°C to 9.19x10^{18} \text{ cm}^{-3} at 320°C). But, decreasing the top heater temperature further to 290°C lead to a sharp increase in carrier concentration and decrease in mobility. This was likely due to the VI/V ratio becoming too large, leading to Se_{Bi} antisite vacancies acting at double donors and increasing the carrier concentration. A high VI/V ratio was likely also the cause of an increased misaligned platelet density at lower top heater temperatures (290-320°C). But, at the high end of the top heater temperature range (>400°C), the platelet density also increased, likely due to increasing growth rates with higher top heater temperature. The growth rate dependence on temperature was likely a diffusion-controlled relationship. Since the decrease in carrier concentration at lower temperatures was accompanied by a steady structural quality (Rocking curve FWHM = 0.0475 at 290°C, = 0.0462 at 500°C), the selenium vacancy concentration appears to be the dominant factor in the change in carrier concentration and mobility over this range. This trend was even unaffected by a growth rate-induced increase in surface roughness (1.28 nm at 500°C, 5.10 nm at 290°C) while the carrier concentration decreased.

Increasing the bottom heater temperature increased the selenium partial pressure over the range studied (200-280°C), leading to an increase in the effective VI/V ratio, an increase in growth rate, and lowering of the the carrier concentration from 3.72x10^{19} \text{ cm}^{-3} at 200°C to 6.5x10^{18} \text{ cm}^{-3} at 280°C. However, as the bottom heater temperature increased,
the misaligned platelet density increased until at 280°C, the entire surface was covered in misaligned platelets and other crystallographic orientations were even present. While an increase in platelet density also accompanied large VI/V ratios in the top heater study, the present of non c-axis oriented planes at 280°C is likely due to this increased substrate temperature allowing a partial overcoming of the weak van der Waals bonds by which Bi$_2$Se$_3$ adheres to the substrate. It was likely not a growth rate effect since halving the growth rate at 280°C did not decreased the platelet density significantly. The higher platelet density and multiple orientations were the likely cause of a decreased in electron mobility above 260°C even with a lower carrier concentration.

Using the two heater system allowed for independent control of the Se evaporation temperature and TMBi decomposition temperature and depositing epitaxial thin films of Bi$_2$Se$_3$ exhibiting 6-fold rotational symmetry and high quality rocking curve data (FWHM <0.05° for (006) peak). A high effective VI/V ratio was shown to be critical for decreasing the carrier concentration in Bi$_2$Se$_3$ and improving mobility. However, increasing the Se partial pressure by increasing the susceptor temperature also increases the substrate temperature, which was shown to be detrimental to crystal quality and carrier mobility, either due to an overly large VI/V ratio or a higher substrate temperature leading to the nucleation of other crystallographic orientations. Being able to independently control the Se supply and substrate temperature may allow keeping a high VI/V ratio while also minimizing the misaligned platelet density. HPCVD also has the disadvantage of not being able to “turn off” the selenium source, preventing bi-layer growth and junctions with other materials. This will be explored in the next chapter be using MOCVD to deposit Bi$_2$Se$_3$ thin films.
4.5 References

17. L. E. Dodd, Journal of the American Chemical Society, 42, 8, 1579 (1920)
Chapter 5  
Metal-Organic Chemical Vapor Deposition Growth of Bi\textsubscript{2}Se\textsubscript{3} Thin Films

5.1 Introduction

Because HPCVD uses a solid selenium source immediately around the substrate, it is not possible to separate the substrate temperature from the selenium source temperature. Also, it is not possible to control the introduction of Se to the substrate since it gradually is introduced as the susceptor heats. In order to separate the substrate temperature from the Se evaporation temperature, and also to allow the growth of bi-layer structures with other materials, MOCVD using two metal organic sources was studied in depth. MOCVD has been previously used in a very limited way to deposit Bi\textsubscript{2}Se\textsubscript{3} for thermoelectric applications. However, films were polycrystalline with poor electrical properties compared to MBE and HPCVD growth (CC = 2x10\textsuperscript{19} cm\textsuperscript{-3} and mobility = 250 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}).\textsuperscript{1} This was likely due to using Pyrex as a substrate and also due to the high substrate temperatures used (450-550°C). Substrate temperatures above 250°C were shown to cause polycrystalline growth using HPCVD. Using the same two-heater setup that was used for HPCVD growth, the top heater was used to decompose both trimethylbismuth (TMBi) and dimethylselenide (DMSe) and the bottom heater was used to keep the substrate at an appropriate temperature. It was hoped that by separating the substrate temperature from the selenium supply, greater flexibility in controlling the substrate temperature and VI/V ratio in order to achieve epitaxial Bi\textsubscript{2}Se\textsubscript{3} thin films with lower carrier concentration would be achievable. In addition, this arrangement would
permit the growth of multiple layers of different materials, something that would be impossible with the solid Se source in close proximity to the substrate at elevated temperatures. The MOCVD growth procedure was discussed in greater detail in section 3.4.2.

The first goal of this study was to achieve the growth of the proper phase, Bi$_2$Se$_3$. After this was achieved, understanding the effects of different growth conditions on the structural and electrical properties of Bi$_2$Se$_3$ was studied, mainly the total flow rate of hydrogen through the chamber, the substrate temperature (now separated from the selenium source temperature), and the selenium to bismuth (VI/V) ratio. After these were studied, two modified growth processes were studied, namely pulsed growth, wherein the TMBi source was turned on and off at set intervals, and a growth which attempted to mimic HPCVD growth by introducing the DMSe source as the susceptor heated.

5.2 Initial Studies of Bi$_2$Se$_3$ Deposition

The first set of experiments essentially reproduced the parameters used for HPCVD growth while introducing a small flow of DMSe instead of the solid selenium source. A growth of 5 minutes was completed using a top heater temperature of 375°C and a bottom heater temperature of 220°C with a TMBi flow rate of 0.34 sccm and a DMSe flow rate of 2.69 sccm with a resulting VI/V ratio of 8. XRD performed on this sample only showed peaks for the substrate and elemental Bi as seen in Figure 5-1(a). This is evidence that this temperature is insufficient to decompose the DMSe that was
present, resulting in a lack of Se available at the surface. The top heater temperature was increased to 500°C in order to decompose DMSe more readily.

Figure 5-1. XRD for samples grown with top heater temperature of (a) 375°C, showing only Bi deposition and (b) 500°C, showing Bi$_2$Se$_3$ deposition.
As noted in chapter 4, this also increases the supply of Bi at the substrate, so the TMBi flow rate was reduced to 0.14 sccm. As can be seen in Figure 5-1b, this increase in temperature resulted in the deposition of Bi$_2$Se$_3$ because DMSe was more readily decomposed at a top heater temperature of 500°C.

5.3 Hydrogen Flow Rate

The total H$_2$ flow rate through the growth chamber was then studied to determine its effect on growth. The H$_2$ flow rate changes the residence time of the metal-organic precursors, thereby affecting the supply of the metal-organic sources at the substrate. Using the growth conditions outlined in Table 1, growths were performed with H$_2$ flow rates through the chamber ranging from 30-1000 sccm. The H$_2$ flow rate had a significant impact on the growth rate and electrical and structural properties of the films. The most important change, which was likely the cause of all the other changes seen, was an increased growth rate with increased H$_2$ flow rate, as seen in Figure 5-2. The growth rate increased from 3.9 nm/min at 30 sccm to 12.1 nm/min at 100 sccm to 22.8 nm/min at 1000 sccm. The growth rate appears to follow a logarithmic dependence on H$_2$ flow rate. But, it also looks similar to the dependence changing from mass transport-controlled to surface kinetics-controlled growth. While the 30 sccm growth rate of 3.9 nm/min is comparable to those seen in HPCVD growth, the others are much greater than what was usually seen using HPCVD. A summary of the structural and electrical properties of these films can be found in Table 2.
Table 5-1. Growth Conditions for H₂ Flow Rate Study

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ Flow Rate (scm)</td>
<td>30-1000</td>
</tr>
<tr>
<td>Top Heater Temperature (°C)</td>
<td>500</td>
</tr>
<tr>
<td>Bottom Heater Temperature (°C)</td>
<td>220</td>
</tr>
<tr>
<td>TMBi Flow Rate (scm)</td>
<td>0.14</td>
</tr>
<tr>
<td>DMSe Flow Rate (scm)</td>
<td>14.16</td>
</tr>
<tr>
<td>Chamber Pressure (Torr)</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 5-2. Growth rate dependence on H₂ flow through chamber with logarithmic fit with $R^2 = 0.988$. 

\[ y = -12.896 + 11.903 \log(x) \]

\[ R^2 = 0.98811 \]
Table 5-2. Electrical and Structural Properties of Films Grown with Varying H₂ Flow Rate

<table>
<thead>
<tr>
<th>H₂ Flow Rate (sccm)</th>
<th>30</th>
<th>100</th>
<th>500</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier Concentration (cm⁻³)</td>
<td>6.73x10¹⁹</td>
<td>4.25x10²⁰</td>
<td>9.55x10²⁰</td>
<td>3.97x10²²</td>
</tr>
<tr>
<td>Mobility (cm²V⁻¹s⁻¹)</td>
<td>155</td>
<td>19.9</td>
<td>11.5</td>
<td>15.4</td>
</tr>
<tr>
<td>Growth Rate (nm/min)</td>
<td>3.9</td>
<td>12.2</td>
<td>18.7</td>
<td>22.84</td>
</tr>
<tr>
<td>(006) FWHM (°)</td>
<td>0.047</td>
<td>1.80</td>
<td>1.17</td>
<td>1.38</td>
</tr>
<tr>
<td>Polycrystalline?</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

The increase in growth rate was accompanied by a decline in structural quality. While the sample grown with an H₂ flow rate of 30 sccm showed epitaxial growth with 6-fold rotational symmetry and only the (003) family of reflections present in a theta-2theta scan, films with higher flow rates showed polycrystalline behavior. As can be seen in Figure 5-3, while the sample grown with a lower flow rate (30 sccm) shows the (003) family of peaks, even increasing the flow to 100 sccm leads to other peaks being present. Increasing the flow to 500 and 1000 sccm also results in polycrystalline growth with no 6-fold rotational symmetry.
Figure 5.3  Theta-2theta XRD scan of samples grown with H\textsubscript{2} flow rates of (a) 30 and (b) 100 sccm.  30 sccm scan shows only (003) family of peaks while 100 sccm scan shows multiple other orientations present. (Insert) evidence of 6-fold rotational symmetry for a film grown with 30 sccm H\textsubscript{2} flow rate.

This change in structural quality is also apparent from SEM images (Figure 5.4).

For the lowest flow rate, 30 sccm, the surface is covered in triangular pyramids similar to samples grown with HPCVD (Figure 5.4a). However, increasing the H\textsubscript{2} flow rate, and thus increasing the growth rate, results in a less well-ordered surface, reflecting what is
seen in the XRD results. At H₂ flow rates of 500 and 1000, the surface is covered in large chunks or material, probably indicative of island growth rather than layer-by-layer growth.

Figure 5-4. SEM images of samples grown with (a) 30 sccm, (b) 100 sccm, (c) 500 sccm, and (d) 1000 sccm H₂ flow rate.

The increase in growth rate and decreased in structural quality was also accompanied by an increase in carrier concentration and decrease in mobility. As can be seen in Figure 5-5, while the sample grown with a 30 sccm flow rate has a carrier concentration of 6.7x10¹⁹ cm⁻³ and a mobility of 155 cm²V⁻²s⁻¹, the higher flow rates show a sharp jump in the carrier concentration to 4-9x10²⁰ cm⁻³ and a sharp drop in mobility to 11-20 cm²V⁻¹s⁻¹. The sharp increase in carrier concentration and decrease in mobility accompanies the change from epitaxial growth to polycrystalline growth. This
may be due to the higher growth rates leading to more defects that act as electron donors and the many grain boundaries greatly decreasing the mobility. Because of the sharp decrease in structural and electrical properties at higher flow rates, all subsequent growths were done with a low H$_2$ flow of 30 sccm.

Figure 5-5. (red) mobility and (blue) carrier concentration versus H$_2$ flow rate through growth chamber.

5.4 Substrate Temperature

One advantage of MOCVD growth over HPCVD is the ability to control the substrate temperature independently of the Se supply. The substrate temperature was varied over the range from 190-250°C. Growing much below this temperature range is difficult because of the top heater’s close proximity and effect on the bottom heater
temperature. Other conditions are summarized in Table 3. As can be seen in Figure 5-6, while the samples grown at 190°C and 220°C show the triangular features normal for epitaxial Bi$_2$Se$_3$ growth, increasing the bottom heater temperature to 250°C shows a much less ordered surface. This change was also confirmed by XRD analysis.

![Figure 5-6 Films grown with bottom heater temperature of (a) 190°C, (b) 220°C, and (c) 250°C.](image)

**Table 5-3. Growth Conditions for Substrate Temperature Study**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ Flow Rate (sccm)</td>
<td>30</td>
</tr>
<tr>
<td>Top Heater Temperature (°C)</td>
<td>500</td>
</tr>
<tr>
<td>Bottom Heater Temperature (°C)</td>
<td>190-250</td>
</tr>
<tr>
<td>TMBi Flow Rate (sccm)</td>
<td>0.14</td>
</tr>
<tr>
<td>DMSe Flow Rate (sccm)</td>
<td>14.16</td>
</tr>
<tr>
<td>Chamber Pressure (Torr)</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 5-7 shows the rocking curve for samples grown with a bottom heater temperature of 220°C and 250°C. Accompanying the change in surface quality seen in Figure 5-6, the structural quality also declines. The FWHM of the (006) rocking curve of Bi$_2$Se$_3$ increases from 0.046° at 220°C to 1.18° at 250°C. This may be due to the increase in
substrate temperature leading to a partial overcoming of the weak van der Waals bonding by which $\text{Bi}_2\text{Se}_3$ bonds to the substrate surface. As the growth rates were similar for the growths at 190°C (9.2 nm min$^{-1}$) and 250°C (9.6 nm min$^{-1}$), this was likely not a factor in the change in structural quality. While the sample grown at 250°C still only shows the (003) family of peaks in a theta-2theta scan, this may be related to a similar decrease in crystal quality seen when increasing the substrate temperature in HPCVD growth.

Figure 5-7 Rocking curves of the (006) peak for samples grown with a bottom heater temperature of (a) 220°C (FWHM = 0.046°) and (b) 250°C (FWHM = 1.18°).
The electrical properties also changed significantly when the substrate temperature was increased to 250°C (Figure 5-8). The carrier concentration remained nearly constant at 6-7x10^{19} for substrate temperatures of 190-220°C, but increases significantly to 4x10^{20} cm^{-3} and the mobility decreased from 155 cm^{2}V^{-1}s^{-1} to 23 cm^{2}V^{-1}s^{-1}. This decrease in mobility and increase in carrier concentration may be related to the decrease in structural quality as was seen with increasing H_{2} flow rate above in section 5.3.

![Graph showing mobility and carrier concentration for films grown with varying substrate temperature.](image)

**Figure 5-8.** Mobility and carrier concentration for films grown with varying substrate temperature.

It may also be caused by the increasing substrate temperature leading to decreased selenium incorporation, leading to more selenium vacancies. This was not seen in the HPCVD growths, most likely because the increase in substrate temperature was also accompanied by an increase in the selenium vapor pressure to offset the loss of selenium.
from the Bi$_2$Se$_3$ since these two conditions were linked in HPCVD growth. Since they are controlled independently in MOCVD growth, the increase in substrate temperature may lead to an increase in selenium vacancies without the offsetting increase in selenium vapor pressure.

**Table 5-4. Structural and Electrical Properties for Films Grown with Varying Substrate Temperature**

<table>
<thead>
<tr>
<th>Substrate Temperature (°C)</th>
<th>190</th>
<th>220</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier Concentration (cm$^{-2}$)</td>
<td>7.26x10$^{19}$</td>
<td>6.73x10$^{19}$</td>
<td>3.99x10$^{20}$</td>
</tr>
<tr>
<td>Mobility (cm$^2$V$^{-1}$s$^{-1}$)</td>
<td>115</td>
<td>155</td>
<td>23.1</td>
</tr>
<tr>
<td>(006) FWHM (°)</td>
<td>-</td>
<td>0.046</td>
<td>1.18</td>
</tr>
<tr>
<td>Poly-crystalline?</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Growth Rate (nm min$^{-1}$)</td>
<td>9.2</td>
<td>6.6</td>
<td>9.6</td>
</tr>
</tbody>
</table>

**5.5 VI/V Ratio**

![Figure 5-9. 2x2 μm scans of films grown with a VI/V ratio of (a) 22:1, (b) 44:1, and (c) 80:1](image)

The effective selenium-to-bismuth ratio, or VI/V ratio was shown to be important for reducing the carrier concentration by minimizing selenium vacancies. So, the VI/V
ratio was varied using MOCVD growth by varying the H₂ flow rate through the DMSe bubbler, while keeping the flow through the TMBi bubbler constant. The DMSe flow was varied from 2.7 sccm to 16.8 sccm while maintaining the TMBi flow rate at 0.14 sccm, resulting in a VI/V ratio from 22:1 to 80:1. AFM images for these three films are seen in Figure 5-9. As the VI/V ratio increases, the triangular features become more defined. This is consistent with previous MOCVD growth where increasing VI/V ratio improved crystalline quality. The growth rate remained constant throughout this range of VI/V ratio at ~6.2 nm/min, meaning that DMSe supply is not the rate-limiting factor of film growth. This is also consistent with the previous MOCVD study.

Table 5-5. Growth Conditions for VI/V Ratio Study

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ Flow Rate (sccm)</td>
<td>Top Heater Temperature (°C)</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>Bottom Heater Temperature (°C)</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>TMBi Flow Rate (sccm)</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>DMSe Flow Rate (sccm)</td>
<td>3.08-11.2</td>
</tr>
<tr>
<td></td>
<td>Chamber Pressure (Torr)</td>
<td>100</td>
</tr>
</tbody>
</table>

The electrical properties also changed with increasing VI/V ratio, seen in Figure 5-10. The carrier concentration decreased from 5.5x10²⁰ cm⁻³ at VI/V = 22 to 6.8x10¹⁹ cm⁻³ at VI/V = 44 and 80. The mobility also increases over this range from 16 cm²V⁻¹s⁻¹ at VI/V = 22 to 125 cm²V⁻¹s⁻¹ at VI/V = 44 to 155 cm²V⁻¹s⁻¹ at VI/V = 80. This seems to be a direct result of the VI/V ratio driving down the selenium vacancy concentration. It is notable that the range of carrier concentrations is much larger than what was seen in
the top heater study for HPCVD growth, which was only $9 \times 10^{18} - 1.5 \times 10^{19}$ cm$^{-3}$. The bottom heater HPCVD study had a range from $6.5 \times 10^{19} - 3 \times 10^{19}$ cm$^{-3}$, which is larger, but still a smaller range than the nearly order of magnitude change while varying the VI/V ratio in MOCVD. It also appears that the VI/V ratio’s effect on carrier concentration saturates in the range studied as it remained constant between 44:1 and 80:1 at $6.8 \times 10^{19}$ cm$^{-3}$. These and other properties are summarized in Table 6.

Figure 5-10. Hall mobility and carrier concentration versus VI/V ratio.
Table 5-6. Structural and Electrical Properties for Films Grown with Varying VI/V Ratio

<table>
<thead>
<tr>
<th>VI/V Ratio</th>
<th>22:1</th>
<th>44:1</th>
<th>80:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier Concentration (cm⁻³)</td>
<td>5.50x10²⁰</td>
<td>6.80x10¹⁹</td>
<td>6.73x10¹⁹</td>
</tr>
<tr>
<td>Mobility (cm²V⁻¹s⁻¹)</td>
<td>15.9</td>
<td>122</td>
<td>155</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>31.7</td>
<td>33.1</td>
<td>33.2</td>
</tr>
<tr>
<td>Roughness (nm)</td>
<td>3.53</td>
<td>1.94</td>
<td>1.93</td>
</tr>
</tbody>
</table>

5.7 Pulsed and Modified Growth

5.7.1 Pulsed Growth

The electrical properties of Bi₂Se₃ films grown by MOCVD are markedly poorer than those grown by HPCVD. While HPCVD growth achieved films with carrier concentrations as low as 7.5x10¹⁸ cm⁻³ and mobility as high at 800 cm²V⁻¹s⁻¹ at room temperature, MOCVD films generally had carrier concentrations >4x10¹⁹ cm⁻³ and mobilities around 150 cm²V⁻¹s⁻¹. In order to increase the effective VI/V ratio and reduce the carrier concentration further, a series of pulsed growths were performed. Pulsed growth consisted of switching the flow through the TMBi bubbler on or off every 10 seconds during the growth period. When the flow through the bubbler was turned off, the carrier H₂ then flowed through a bypass valve.
Therefore, the total $\text{H}_2$ flow through the growth chamber was constant throughout the entire growth. Because the electrical properties are sensitive to thickness, a series of growths of different lengths of time were done in order to account for the different growth rates between pulsed and normal growth. MOCVD growths were done for 2, 5, 11, and 20 min for each normal and pulsed growth.

Table 5-7. Growth Conditions for Pulsed Growth Study

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<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$ Flow Rate (sccm)</td>
<td>30</td>
</tr>
<tr>
<td>Top Heater Temperature (°C)</td>
<td>500</td>
</tr>
<tr>
<td>Bottom Heater Temperature (°C)</td>
<td>200</td>
</tr>
<tr>
<td>TMBi Flow Rate (sccm)</td>
<td>0.14</td>
</tr>
<tr>
<td>DMSe Flow Rate (sccm)</td>
<td>11.2</td>
</tr>
<tr>
<td>Chamber Pressure (Torr)</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 5-8. Properties for Samples Grown with Pulsed and Normal MOCVD

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Thickness (nm)</th>
<th>Carrier Concentration (cm$^{-3}$)</th>
<th>Mobility (cm$^2$V$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal (2 min)</td>
<td>18.5</td>
<td>5.4x10$^{19}$</td>
<td>125</td>
</tr>
<tr>
<td>Normal (5 min)</td>
<td>46.8</td>
<td>3.7x10$^{19}$</td>
<td>183</td>
</tr>
<tr>
<td>Normal (11 min)</td>
<td>102.8</td>
<td>4.7x10$^{19}$</td>
<td>164</td>
</tr>
<tr>
<td>Normal (20 min)</td>
<td>157.8</td>
<td>2.8x10$^{19}$</td>
<td>202</td>
</tr>
<tr>
<td>Pulsed (5 min)</td>
<td>24.5</td>
<td>3.7x10$^{19}$</td>
<td>183</td>
</tr>
<tr>
<td>Pulsed (11 min)</td>
<td>42.8</td>
<td>2.2x10$^{19}$</td>
<td>263</td>
</tr>
<tr>
<td>Pulsed (20 min)</td>
<td>74.5</td>
<td>2.8x10$^{19}$</td>
<td>220</td>
</tr>
</tbody>
</table>
5.7.1.1 Hall Measurements

The results of Hall measurements performed on each sample are shown below in Figure 5-11. The mobility of samples grown using pulsed deposition sees a notable trend over the range of thicknesses measured, being higher than for samples grown using normal growth. For both pulsed and normal growth, carrier concentration decreases with increasing thickness. For the range studied, however, the pulsed growth carrier concentrations are lower than the normal growth carrier concentrations. For samples of similar thicknesses, a 43 nm thick pulsed sample had a carrier concentration of $2.27 \times 10^{19}$ cm$^{-3}$ while a 47 nm thick normal growth sample had a carrier concentration of $3.71 \times 10^{19}$ cm$^{-3}$. The same trend is also seen for the mobility, with a mobility $263$ cm$^2$V$^{-1}$s$^{-1}$ for a pulsed sample and $183$ cm$^2$V$^{-1}$s$^{-1}$ for a normal sample, with thicknesses of 43 nm and 47 nm, respectively.

![Graphs showing carrier concentration and mobility versus thickness for pulsed and normal MOCVD growth. The dashed lines are guide lines for the pulsed and normal growth results versus thickness to show dependence on thickness.](image)

Figure 5-11. (a) Carrier concentration and (b) mobility versus thickness for pulsed and normal MOCVD growth. The dashed lines are guide lines for the pulsed and normal growth results versus thickness to show dependence on thickness.
This increase in mobility and decrease in carrier concentration for pulsed versus normal growth may have at least two contributing factors. Turning the TMBi source on and off every 10 seconds effectively increases the VI/V ratio, thereby possibly further driving down selenium vacancies and decreasing the carrier concentration. There was also a significant decrease in the effective growth rate for pulsed growth. The average growth rate for pulsed growth was roughly half of that for normal growth, 4.31 nm/min compared to 8.97 nm/min for normal growth. But, just including the time when the TMBi source was on, the growth rates were essentially equal. This could give the precursors more time to diffuse at the surface, leading to fewer defects in the film. But, as will be shown below, the structural quality of the films was not significantly impacted by pulsed growth. Therefore, it is most likely that the effective VI/V ratio is the main factor in lowering the carrier concentration and increasing the mobility in pulsed growth films.

5.7.1.2 X-Ray Diffraction

XRD measurements were performed on samples grown by normal and pulsed MOCVD growth of similar thicknesses (43 nm for pulsed, 47 nm for normal) compared in section 5.7.1.1. The rocking curve of the (006) peak shows an overlapping broad and sharp peak for both samples (Figure 5-12). The only difference is the ratio of the broad peak to the sharp peak, with the normal growth sample having a more prominent sharp peak compared to the pulsed growth sample. The more prominent broad peak in the pulsed sample does lead to a higher FWHM measurement, 0.1795° compared to 0.0738°
for the normal growth sample. This difference may be due to the slight difference in thickness between these two particular samples or due to random variation between different film growths such as humidity. The rocking curve of the off axis (015) peaks are also not significantly different between normal and pulsed growth, which are 2.2° and 2.5° respectively. This shows that pulsed growth does not have a significant impact on the “twist” of in-plane grains.

Figure 5-12. Rocking curve of the (006) peak for samples grown using (a) normal MOCVD (FWHM = 0.0738°) and (b) pulsed MOCVD (FWHM = 0.1795°).
5.7.2 Modified MOCVD Growth

5.7.2.1 XRD Difference from HPCVD Growth

One notable difference in the structural properties between HPCVD-grown films and MOCVD-grown films is the shape of rocking curve scans of the (006) peaks. HPCVD-grown films exhibit a single sharp peak with a FWHM normally around 0.05 wide. This is consistent over most of the growth conditions studied. MOCVD-grown films, on the other hand, generally have what appears to be a broad peak overlapping with a sharp peak. While the sharp peak generally has a similar FWHM to HPCVD-grown films, the broad peak is generally an order of magnitude wider.

5.7.2.2 Modified MOCVD Process

One significant difference between HPCVD and MOCVD is the timing of the precursors being introduced to the substrate. In MOCVD, both sources can be turned on at the same time and at a set time. For HPCVD, the selenium is gradually introduced to the substrate as the vapor increases while the substrate heats up. The bismuth source is then turned on when the susceptor reaches the intended growth temperature. So, in HPCVD growth, selenium is introduced to the substrate much sooner than the bismuth precursor. In order to help determine whether this plays a role in the different XRD results seen between the two growth methods, an MOCVD run was performed that attempted to simulate more accurately the effects of HPCVD growth. While the bottom heater was heating, the DMSe source was turned on at 100°C and kept on until the
susceptor reached the intended growth temperature (200°C) and the TMBi was then turned on. Other conditions are the same as were used in the pulsed growth study, summarized in Table 5-7.

5.7.2.3 Modified MOCVD Results

The rocking curve of this growth compared to a normal MOCVD growth can be seen in Figure 5-13. The modified MOCVD growth in which the DMSe flow was started as the susceptor heated up (Figure 5-13b) shows a single sharp peak for the rocking curve of the (006) peak, much closer to what is usually seen for an HPCVD growth than a normal MOCVD growth (Figure 5-13a), which has a broad and sharp peak overlapping. This suggests that the introduction of the selenium source to the substrate as it heats, common to both HPCVD growth and the modified MOCVD growth, has an effect on how the Bi$_2$Se$_3$ film grows. It is possible that during normal MOCVD growth, a more disordered layer deposits first on the bare substrate before a more well-ordered layer deposits. But, in HPCVD and the modified MOCVD growth, the selenium introduced to the substrate well before the bismuth source may coat the substrate and act as a buffer layer, allowing immediate well-ordered growth.

The difference in the x-ray data did not have a large impact on the electrical properties of the films grown by the normal and modified MOCVD growth processes. For films of similar thicknesses (47 nm for normal growth, 46 nm for modified growth), the mobilities were very similar (183 cm$^2$V$^{-1}$s$^{-1}$ for normal growth, 162 cm$^2$V$^{-1}$s$^{-1}$ for modified growth). The carrier concentration for the modified MOCVD growth was
lower than that of normal MOCVD ($1.1 \times 10^{19}$ cm$^{-3}$ compared to $3.7 \times 10^{19}$ cm$^{-3}$). This was the lowest carrier concentration recorded for any MOCVD-grown film using normal, pulsed or modified growth. This decrease may be attributed to the more disordered layer seen in normal and pulsed MOCVD growth having more vacancies and other carrier-causing defects.

Figure 5-13. Rocking curve of the (006) peak for sample grown using (a) normal MOCVD and (b) modified MOCVD (turning on the DMSe source as the susceptor heats).
5.8 Deposition on MgB$_2$

MgB$_2$, a superconductor, has been grown using the same HPCVD system used to grow Bi$_2$Se$_3$. This allows the possibility of growing MgB$_2$/Bi$_2$Se$_3$ bilayers without exposure to atmosphere and the risk of oxidation. The HPCVD growth of MgB$_2$ is described in detail in Zeng, et al.\textsuperscript{4} Generally, the MgB$_2$ HPCVD process involves the heating of solid magnesium pellets held in a susceptor around the substrate while B$_2$H$_6$ in H$_2$ flows through the growth chamber and reacts with the magnesium to deposit MgB$_2$. In order to create the MgB$_2$/Bi$_2$Se$_3$ bilayer structures, the MgB$_2$ growth process was performed as usual. Then, the susceptor was cooled to the temperature used for MOCVD Bi$_2$Se$_3$ growth, 200°C. The chamber was pumped to vacuum and then filled with H$_2$ to 100 Torr as the top heater was raised to 500°C. A normal MOCVD growth was performed with growth conditions as summarized in Table 5-9.

Table 5-9. Growth Conditions for Growth on MgB$_2$

<table>
<thead>
<tr>
<th>H$_2$ Flow Rate (sccm)</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Heater Temperature (°C)</td>
<td>500</td>
</tr>
<tr>
<td>Bottom Heater Temperature (°C)</td>
<td>200</td>
</tr>
<tr>
<td>TMBi Flow Rate (sccm)</td>
<td>0.14</td>
</tr>
<tr>
<td>DMSe Flow Rate (sccm)</td>
<td>14.16</td>
</tr>
<tr>
<td>Chamber Pressure (Torr)</td>
<td>100</td>
</tr>
</tbody>
</table>

Analysis of the structural properties of the Bi$_2$Se$_3$ film deposited on MgB$_2$ show that while Bi$_2$Se$_3$ was deposited successfully, the film quality is markedly poorer than for films grown on sapphire. As seen in Figure 5-14, in addition to the peaks for the SiC
substrate and the MgB\textsubscript{2} layer, the (003) and (006) peaks for Bi\textsubscript{2}Se\textsubscript{3} are clearly visible, but are very weak. A rocking curve of (006) peak of Bi\textsubscript{2}Se\textsubscript{3} barely registers above the background noise (Figure 5-14b).

**Figure 5-14.** (a) Theta-2theta scan of Bi\textsubscript{2}Se\textsubscript{3}-MgB\textsubscript{2} bi-layer on SiC substrate. (b) rocking curve of (006) peak of Bi\textsubscript{2}Se\textsubscript{3}.
The film surface, as seen in an SEM image in Figure 5-15, shows a much rougher surface than seen in MOCVD growth on sapphire. The film appears to be polycrystalline with overlapping grains and flakes rather than an epitaxial film. Other orientations do not show up in the XRD scan. But, this is likely because even the most intense peaks, (003) and (006), barely register above the background noise. This polycrystalline film is likely due to an un-passivated substrate surface. While MgB$_2$ does have a hexagonal structure, the inter-plane bonding is closer to metallic bonding$^5$, therefore it does not grow by van der Waals epitaxy. The surface then may have dangling bonds that can cause Bi$_2$Se$_3$ platelets to grow perpendicular to the substrate surface, rather than in the preferred c-axis oriented growth. Passivation of the MgB$_2$ surface before growth can be studied in greater detail and may alleviate this problem.

Figure 5-15. SEM image of Bi$_2$Se$_3$ film grown on MgB$_2$ by MOCVD.
5.9 Summary

Epitaxial thin films of Bi$_2$Se$_3$ were successfully deposited using MOCVD. There are several key factors for the successful epitaxial growth of Bi$_2$Se$_3$ by MOCVD. A growth rate of <10 nm/min seems essential for c-axis oriented growth. For higher growth rates, multiple orientations were seen in XRD scans with a large increase in rocking curve FWHM, a nearly order-of-magnitude increase in carrier concentration, and a sharp decrease in carrier mobility. It seems for MOCVD growth that the structural properties have a large effect on the electrical properties. These high growth rates likely lead to insufficient diffusion at the surface and the nucleation of multiple crystal orientations, increasing the number of grains and causing an increased vacancy concentration. This higher vacancy concentration then leads to an increased carrier concentration.

The substrate temperature was also found to be important for MOCVD growth. Unlike with HPCVD growth, the substrate temperature and selenium supply can be independently controlled. The effect of substrate temperature from 190-220°C on the film surface and on the electrical properties is negligible. Growing much lower than this is difficult due to the top heater’s effect on the bottom heater due to their close proximity. However, increasing the bottom heater temperature to 250°C shows a large increase in the rocking curve FWHM and increase in carrier concentration, coupled with a large decrease in mobility. The decrease in crystal quality may be attributed to the increase in substrate temperature leading to a partial overcoming of the weak van der Waals forces by which Bi$_2$Se$_3$ bonds to the substrate surface. However, a similar decrease in crystal quality is not seen in HPCVD even until a substrate temperature of 280°C. The increase
in carrier concentration may be caused by the increased substrate temperature leading to a higher vapor pressure of selenium over Bi$_2$Se$_3$, leading to a higher selenium vacancy concentration. The reason a similar increase in carrier concentration was not seen when increasing the substrate temperature in HPCVD growth is that increasing the substrate temperature also increased the selenium supply. And since the vapor pressure over selenium is higher than the vapor pressure of selenium over Bi$_2$Se$_3$, increasing the substrate temperature, and thus the vapor pressure of selenium over Bi$_2$Se$_3$ was offset by the increased selenium supply from the solid selenium source.\textsuperscript{6}

The VI/V ratio was more easily studied independently of other parameters, namely substrate temperature, using MOCVD. A VI/V ratio of up to 80:1 was shown to give the best electrical properties. The higher VI/V ratio lead to more defined triangular features on the surface, consistent with previous MOCVD growth linking VI/V ratio and crystalline quality, evidenced by other misoriented planes present at lower VI/V ratios.\textsuperscript{iii} It also lead to a decrease in carrier concentration and increase in mobility. This is likely simply due to a higher Se vapor pressure over the film leading to a decreased selenium vacancy concentration. This is also consistent with previous MOCVD growth of Bi$_2$Se$_3$. However, the VI/V ratio at which the electrical properties level out is higher than seen in previous MOCVD growth, possibly due to a different selenium precursor being used.\textsuperscript{iii}

Pulsed growth was shown to have a significant impact on the electrical properties of Bi$_2$Se$_3$. Films grown by the pulsed method have on average lower carrier concentration and higher mobility than films of similar thickness grown using the normal method. The pulsed growth also cut the growth rate essentially in half. But, it had a negligible effect on the structural properties of the film, with similar rocking curve data
for both pulsed and normal growth. Since the structural properties were so similar, the improvement in electrical properties can be attributed to an effective increase in the VI/V ratio due to the TMBi supply being turned off and on every 10 seconds, but having the DMSe supply remain constant. The best electrical properties were obtained using pulsed growth (TMBi on for 10 seconds, then off for 10 seconds) for a sample that was 43 nm thick and had a carrier concentration of $3.21 \times 10^{19}$ cm$^{-3}$ and a mobility of 275 cm$^2$V$^{-1}$s$^{-1}$.

The modified MOCVD process, in which the DMSe source was turned on while the substrate was still heating, helped to partially simulate the conditions involved in HPCVD growth. The additional selenium may act as a buffer layer that allows for a more well-ordered growth immediately without a more disordered layer as is seen in the XRD for normal MOCVD films. This does not seem to significantly affect the mobility, but does decrease the carrier concentration from $3.7 \times 10^{19}$ to $1.1 \times 10^{19}$ cm$^{-3}$. This may be because the more disordered layer includes more vacancies and other carrier-causing defects.
5.10 References


Chapter 6
Atmospheric Effects on the Surface of Bi$_2$Se$_3$

6.1 Introduction

Recently, attention has been paid to the degradation of Bi$_2$Se$_3$ due to environmental exposure which leads to an increase in conductivity. Band bending near the surface has been observed in Bi$_2$Se$_3$ with angle-resolved photoemission spectroscopy after several hours of exposure to ambient air.$^1$ The band bending was attributed to several effects including the incorporation of impurity atoms into lattice sites$^2$ adsorption of gas impurities on the surface$^3$ and surface oxidation$^4$. The band bending results in an accumulation layer of negative charge at the surface. The accumulation layer, while independent of the topological surface states$^7$, must be distinguished from them in transport measurements to accurately characterize the surface states. The increase in conductivity has been observed upon exposure to air$^5$, CO$^6$, H$_2$O$^7$, and O$_2$$^8$. H$_2$O in particular has been shown to induce surface states similar to those that develop in a sample cleaved in air and then measured in vacuum.$^7$ On the other hand, O$_2$ has been suggested to be a compensating p-type dopant$^8$, filling selenium vacancies and therefore resulting in a decrease in conductivity. In other studies, however, O$_2$ has been shown to alter the surface states and decrease spin current$^4$.

It is difficult to avoid exposing the surface of Bi$_2$Se$_3$ films to ambient air during sample handling and characterization. As a result, further studies are needed to understand the effects of the components of ambient air (H$_2$O, O$_2$ and N$_2$) on the
chemistry and electrical characteristics of the Bi$_2$Se$_3$ surface and determine the time frame over which changes occur in order to identify suitable conditions for sample handling. In the first set of experiments, time-dependent Hall-effect measurements were carried out on a series of Bi$_2$Se$_3$ films grown under nominally the same conditions under different ambient environments, specifically air, nitrogen, water vapor in nitrogen, and oxygen. The measured changes in resistivity, electron concentration and electron mobility over time under each of the environments was then used in combination with X-ray photoelectron spectroscopy (XPS) to better understand the relationship between electrical properties and changes in the surface chemistry of Bi$_2$Se$_3$.

6.2 Experimental Setup

Bi$_2$Se$_3$ films were grown using the HPCVD process described in chapter 4. Films were grown with a lower heater temperature of 220°C and an upper heater temperature of 375°C at a growth pressure of 100 Torr. Typical room temperature carrier concentrations were n = 7.5x10$^{18}$-1x10$^{19}$ cm$^{-2}$ and Hall mobilities were $\mu$ = 350-450 cm$^2$V$^{-1}$s$^{-1}$ for this set of films. After film growth, the samples were removed from the CVD reactor and immediately placed in the Hall measurement system, which was isolated from the surrounding environment. Except for the sample simply held in air, a purge gas of either N$_2$, water vapor carried in N$_2$, or O$_2$ was passed through the Hall system enclosure at a flow rate of approximately 1.5 slm. For more detail Measurements were taken at set intervals of time, initially every 10 minutes, and then every 20 minutes to several hours as the measurements leveled off. The results were then plotted in order to show how the
films reacted over time in each ambient environment. This Hall measurement setup is discussed in more detail in section 3.4.3.

For the X-ray photoelectron spectroscopy measurements, a sample was placed into the vacuum chamber soon after growth (about 10 min). The system was pumped down and measurements were then taken. For samples held in air, N\textsubscript{2}, and O\textsubscript{2}, the sample was held in the one gas for 2-3 hour before being placed into the vacuum XPS system, pumped down and measured. These samples were then removed from the system, exposed to the same gas for another 2-3 days, then pumped down and measured again. More information can be found in section 3.5.5

6.3 Experimental Results

6.3.1 Hall Data

6.3.1.1 Sample in Air

Figure 6-1 shows the variation in the carrier concentration, mobility, and resistivity of the Bi\textsubscript{2}Se\textsubscript{3} film in air over a period of 30 hours. As can be seen in Figure 6-1a, the resistivity initially increases from 1.86x10\textsuperscript{-3} Ω-cm, peaks after roughly 1 hour at 2.06x10\textsuperscript{-3} Ω-cm, then decreases significantly before leveling out after about 10 hours at 1.73x10\textsuperscript{-3} Ω-cm. This is caused by the changing carrier concentration and mobility as can be seen in Figure 6-1b. The carrier concentration decreases initially from a value of 7.5x10\textsuperscript{18} cm\textsuperscript{-3} to 7.0x10\textsuperscript{18} cm\textsuperscript{-3}, and then increases significantly before leveling out after
about 10 hours at a value of over $9.5 \times 10^{18}$ cm$^{-3}$. This is roughly the same behavior seen previously for a sample left in air, albeit on a shorter time scale. These results show how a Bi$_2$Se$_3$ film reacts to exposure to air over time and act as a baseline in our study of different environments.

Figure 6-1. (a) Resistivity versus time and (b) carrier concentration and Hall mobility versus time for Bi$_2$Se$_3$ film held in air. (c) Sheet density for sample held in air from Brahlek, et al. for comparison to (b).
6.3.1.2 Sample in Nitrogen

The same measurements were done on samples held in different ambient environments, starting with N\textsubscript{2}. The behavior of the carrier concentration of the sample held in N\textsubscript{2} (Figure 6-2a) is significantly different than of the sample held in air. After a small decrease (8\%) in carrier concentration, it reaches a minimum after 2 hours. Approximately the same value is observed at 20-30 hours after growth. This decrease may be due to residual air in the chamber leading to oxygen incorporation before the ambient is completely N\textsubscript{2}. The chamber may not be immediately evacuated of all air when the measurements begin. In a corresponding manner, the mobility increases slightly, about 5\%, as the carrier concentration decreases.

6.3.1.3 Sample in Water Vapor

The carrier concentration of a sample held in water vapor can also be seen in Figure 6-2a. The behavior of a sample in water vapor is very similar to the behavior of a sample in air, with a decrease of about 8\% in less than an hour before a 30\% increase after 10 hours. This is very different from the behavior of a sample in N\textsubscript{2}. This implies that water vapor plays a significant, if not the most significant, role in the behavior seen in air. This is also evidenced by the fact that the mobility for a sample held in water vapor changes much in the same way as for a sample held in air. Once the carrier concentration begins to increase significantly after about an hour, the mobility decreases significantly, dropping about 15\% after 10 hours.
6.3.1.4 Sample in Oxygen

The last Hall measurement set was done using a sample held in O₂ gas. As can be seen in Figure 6-2, the carrier concentration decreases to a level far below any of the other samples, a roughly 20% decrease when a minimum is reached after 2 hours. The
carrier concentration then increases significantly, about 15% above the initial value, but not as much as in the water vapor and air samples.

### 6.3.1.5 Analysis of Hall Data

This large decrease may be explained by oxygen filling Se vacancies and acting as a p-type dopant. The charge resulting from a selenium vacancy is \(-2\) according to the equation: \(Se_{Se} \rightarrow V_{Se}^- + Se(g) + 2e'\). An oxygen molecule can then fill this vacancy and capture two free electrons: \(V_{Se}^- + O_2(g) + 2e' \rightarrow O_{2Se}\). The eventual increase in carrier concentration may be attributed to oxidation, as illustrated schematically in Figure 6-3. Both the smaller increase in carrier concentration and the longer time to reach a minimum in the oxygen compared to the air and water vapor samples may be attributed to the oxidation occurring more rapidly when assisted by H\(_2\)O. The sample held in oxygen experiences more incorporation of oxygen-leading to decreased carrier concentration-before oxidation begins to have a large effect on the surface. This is in comparison to the samples held in air and water vapor, which experience a small decrease that may be due to incorporation of oxygen, but oxidize more quickly and lead to n-type doping due to reaction of water vapor with Bi\(_2\)Se\(_3\) resulting in free electrons. Furthermore, the large initial decrease in carrier concentration observed in O\(_2\) is not accompanied by an increase in mobility. The electron mobility drops slightly, <5%, when the carrier concentration reaches a minimum, then drops significantly, 12%, after 10 hours, similar to the sample held in air and water vapor. That the mobility doesn’t increase with the initial decrease in carrier concentration may be because that drop in
carrier concentration is due to oxygen incorporation, which would still lead to an increased density of scattering sites to accompany the decreased carrier concentration.

Figure 6-3. Schematic of proposed oxidation method in oxygen. (a) Bi₂Se₃ with selenium vacancies, (b) oxygen molecules fill vacancies, acting at p-type dopants and lowering carrier concentration, (c) oxygen eventually forms oxide, leading to increase in carrier concentration.

6.3.2 X-Ray Photoemission Spectroscopy

In order to further understand the results seen in the Hall measurements, X-ray photoelectron spectroscopy (XPS) was carried out on samples held in several different environments in order to determine the type and bonding configuration of elements on the surface of the film. An initial measurement was done on a sample as soon it was taken out of the growth chamber. The time before the sample was placed in the XPS chamber was roughly equivalent to the time before the first Hall measurements were taken for the previous samples. Measurements were then taken on samples that had been held in air, N₂, and O₂ for 2-3 hours before being placed in the XPS chamber and pumped down to ultra-high vacuum. After being measured, the same samples were then again
held in their respective ambient environments for 2-3 days before another measurement was taken.

The XPS results of the sample held in air can be seen in Figure 6-4a. The BiO\textsubscript{x} peak increases in area over time while the Bi 4f peak decreases. Similar behavior can be seen for the Se 3d peak (Figure 6-4b). This is consistent with previously reported XPS results for Bi\textsubscript{2}Se\textsubscript{3} held in air.\textsuperscript{10} This gives support to the idea that it is oxidation that gives rise to the increased carrier concentration seen for a sample held in air after several hours then an even larger increase after several days. The XPS results for the sample held in N\textsubscript{2} can be seen in Figure 6-4c and d. As opposed to the sample held in air, there appears to be no growth in the BiO\textsubscript{x} peaks over time. This is consistent with the Hall data showing no significant increase in carrier concentration over time. The sample held in O\textsubscript{2} can be seen in Figure 6-4e and f. After a couple of hours, there was no significant increase in the BiO\textsubscript{x} peaks. However, after a couple of days, there was a slight increase in the BiO\textsubscript{x} peaks even though there was no discernible SeO\textsubscript{x} peak developing (Figure 6-4f). This is not immediately visible from the graph, but analyzing the peak fits of the Bi 4f and BiO\textsubscript{x} peaks shows that from a couple of hours to a couple of days, the area of the BiO\textsubscript{x} peak increases by 23% and the area of the Bi 4f peak decreases by 8%. This shows that there is an increase in oxidation after a period of several days. This increase, however, is not nearly as large as the increase seen in air after several days. This is consistent with the Hall measurements that show an increase in the carrier concentration after a couple of days, but not to the extent seen in the sample held in air. The lack of discernible SeO\textsubscript{x} peaks for a sample held in O\textsubscript{2} even though BiO\textsubscript{x} peaks are present is consistent with previous results, which show BiO\textsubscript{x} peaks developing before SeO\textsubscript{x} peaks.\textsuperscript{12}
Figure 6-4. XPS data for samples held in different ambient environments, (a) Bi peaks and (b) Se peaks for sample in air, (c) Bi peaks and (d) Se peaks for samples held in nitrogen, and (e) Bi peaks and (f) Se peaks for sample held in oxygen.

If oxygen filling selenium vacancies is the cause of the decrease in carrier concentration seen from the Hall data of the sample left in O₂, then the XPS data should
show an increase in the oxygen peak after a couple of hours, corresponding to the minimum in the carrier concentration of the Hall data, but not an increase in the BiO\textsubscript{x} peak, meaning the incorporation of molecular oxygen into lattice vacancies.\textsuperscript{13} The oxygen molecule bonds to the surrounding Bi atoms, reclaiming free electrons caused by the vacancy, but the oxygen atoms remain bonded to each other.\textsuperscript{14} Half of this is seen in the XPS data (Figure 6-5a). There is no discernible increase in the BiO\textsubscript{x} peak after a couple hours compared to an as-grown sample. However, there is also no discernible increase in the oxygen peak (Figure 6-5b). This does not necessarily disprove the theory, however. Placing the sample in the XPS chamber does not freeze the sample in time obviously. The time it takes to pump the sample down to UHV can have an effect on the surface. It is possible that most of the oxygen that diffuse into the sample during the first couple of hours may leave the surface during the time it takes to pump down to UHV. The amount of oxygen incorporation may also be below the instrument detection limit. The system limit is about 0.1%. If oxygen incorporation is on the order of the carrier concentration \((8 \times 10^{18} \text{cm}^{-3})\), then this is below the detection limit. Due to the nature of the experiment, this cannot be definitely determined.

As can be seen in Figure 6-5, there is an oxygen peak present for the sample held in O\textsubscript{2} for a couple of days. This is in comparison to the sample held in N\textsubscript{2}, for which there is no discernible oxygen peak. The molecular oxygen peak for the sample held in O\textsubscript{2} is surprisingly significantly smaller than for the peak held in air. This seems to imply that even in a pure O\textsubscript{2} environment, oxygen is less likely to incorporate into the film or form an oxide than the water vapor present in air.
Figure 6-5. Comparison of (a) Bi peaks and (b) oxygen peaks for samples held in different ambient environments.

6.3.3 Angle Resolved Photoemission Spectroscopy

Angle resolved photoemission spectroscopy (ARPES) is a versatile technique to characterize topological surface states of topological insulators (TI) and many TI systems have been studied using APRES\textsuperscript{15,16}. By changing the orientation of the Brillouin zone with respect to the incident photons, different spatial portions of the Brillouin zone can be probed and a clear band picture with dispersion of the bulk valence band (BVB), topological surface states (TSS) and the bulk conduction band (BCB) can be observed.

ARPES measurements were performed on samples stored and shipped in nitrogen and in air to compare the effect of the ambient environment on the topological surface states. The films tested were grown using HPCVD with conditions similar to those described in section 6.2. The instrumentation used is described in section 3.5.6 of the experimental procedure chapter. The samples were shipped from Penn State University
to North Carolina State University for ARPES measurements performed by Raj Kumar of
Frank Hunte’s research group in the Department of Materials Science and Engineering.
Before shipping, samples were stored in vacuum-sealed plastic bags, but only to a
vacuum of approximately 1 Torr. The difference between the samples was that vacuum
bag of one set of samples was purged with N₂ for 30 sec before being pumped down and
sealed, while the other was not. The time between sealing and measurement was 1-2
weeks for each set of samples.

XPS measurements were carried out on samples from the sets stored and shipped
in N₂ and in air. The results were consistent with those seen in section 6.2.3 with clear
oxygen peaks seen for samples held in a low vacuum of air and no oxygen peaks seen for
samples held in a low vacuum of N₂. ARPES measurements were then performed on
samples from each set. In the band dispersion diagram of a Bi₂Se₃ thin film stored in N₂,
TSS are clearly visible in between the bulk valence band (BVB) and the bulk conduction
band (BCB) for the sample held in N₂ (Figure 6-6a). When the sample was rotated to scan
different portions of the Brillouin zone, the TSS intensity changed with respect to the
incident photoelectrons thereby confirming the spatial distribution of TSS in the Brillouin
zone.

As demonstrated by the Hall measurements, the samples are n-doped and the
ARPES confirmed that the Fermi level lies in the BCB. In the case of the sample held in
air, the Fermi level lies in the BCB but no TSS was observed (Figure 6-6b) which is
likely due to the oxidation of Bi₂Se₃ surface into BiOₓ as indicated by XPS. ARPES is a
very surface sensitive technique and can’t detect TSS if there is an oxidized BiOₓ layer
on the Bi₂Se₃ thin films. These measurements show that it is possible to protect the TSS
of Bi$_2$Se$_3$ over extended periods of time by storing the samples in an inert environment that does not contain water vapor.

Figure 6-6. ARPES measurements with varying incident angle -6° to +6° for a sample stored in (a) N$_2$ and in (b) air.
6.4 Summary

In conclusion, the type of ambient environment significantly impacts the electrical properties of Bi$_2$Se$_3$ thin films. Given the similarity between the behavior of the Hall measurements of a film held in air and one held in water vapor, it is clear that water vapor plays the most significant role in the changes in the electrical properties of samples left in air. The XPS data backs up the theory that this change is due mostly to oxidation of the Bi$_2$Se$_3$ surface. Exposure to pure oxygen results in a small increase in oxidation after several days, but not nearly to the extent seen in the air sample. The presence of oxidation is significantly less for a sample held in pure O$_2$ compared to a sample held in air. Nitrogen has very little effect on the surface of Bi$_2$Se$_3$. A small decrease in carrier concentration was seen over a couple of hours, but then the carrier concentration remained constant. No oxidation was seen in the XPS data for a sample held in N$_2$. Prolonged exposure to air was also found to significantly affect the measurement of topological surface states. ARPES measurements on samples held in air and N$_2$ showed that the ambient environment can even impact the ability to detect topological surface states. Clearly, the storage and handling of Bi$_2$Se$_3$ is of significant importance in researching topological insulating behavior and applications, with storage in N$_2$ being a good way to preserve surface quality by limiting exposure to O$_2$ and water vapor.
6.5 References

Chapter 7
Summary and Future Work

7.1 Summary

The prediction and demonstration of 2D and 3D topological insulator materials has prompted much research into their growth and characterization. Among other potential applications is the hope that the study of topological insulators could lead to the confirmation of Majorana fermions, which could be harnessed in quantum computing. In order to aid in the study of topological insulators, particularly Bi$_2$Se$_3$, epitaxial thin films of Bi$_2$Se$_3$ were fabricated using two main methods, HPCVD and MOCVD. HPCVD in particular has the potential for a large VI/V ratio, useful for minimizing the carrier concentration in Bi$_2$Se$_3$.

7.1.1 HPCVD

A new method for the growth of Bi$_2$Se$_3$, HPCVD, was developed which allows for a high VI/V ratio of selenium to bismuth by having a solid selenium source in close proximity to the substrate. This technique had previously been used in a similar manner to grow MgB$_2$. A high effective VI/V ratio was shown to be important for minimizing carrier concentration and maximizing carrier mobility. A two heater setup was developed to decompose TMBi at a higher temperature than is optimal for the evaporation of selenium. Too high of a VI/V ratio, however, led to an increase in the concentration of
misaligned platelets and even to an increase in carrier concentration, likely due to Se\textsubscript{Bi} antisite defects. Despite changes in film structure, such as increases in misaligned platelet density and grain size, the main factor affecting the electron mobility was the carrier concentration. As the carrier concentration increased, the mobility decreased and vice versa. This indicates that ionized impurity scattering is the dominant factor affecting the mobility in HPCVD-grown films. As the concentration of ionized selenium vacancies increases, the interaction of carriers with these impurities increased, resulting in a decrease in the Hall mobility. Increasing the VI/V ratio by increasing the selenium source temperature also increases the substrate temperature. Above 240°C, this caused the deposition of crystallographic orientations other than the preferred c-axis oriented direction. These elevated temperatures allowed for a partial overcoming of the weak van der Waals bonding essential for van der Waals epitaxy growth of Bi\textsubscript{2}Se\textsubscript{3}. After optimization, films with a carrier concentration of \(\sim 8 \times 10^{18} \text{ cm}^{-3}\) and room temperature mobility of up to 800 cm\(^2\)V\(^{-1}\)s\(^{-1}\) were demonstrated. These films had a rocking curve FWHM of the (006) peak of \(<0.050^\circ\). A disadvantage of HPCVD growth is the inability to decouple the substrate temperature from the selenium source temperature. Misaligned platelets on the surface could also cause problems for gating and interfacing with other materials.

7.1.2 MOCVD

MOCVD growth of Bi\textsubscript{2}Se\textsubscript{3} thin films was also studied. Decoupling of the substrate temperature from the selenium source allowed for more precise control of these
two parameters. Again, the two heater setup allowed the metal-organic precursors to be decomposed at a much higher temperature than was used for substrate temperature. A substrate temperature below 250°C was shown to be necessary for high quality growth. At 250°C, structural quality decreased and carrier concentration increased to over $1 \times 10^{20}$ cm$^{-3}$. A high VI/V ratio was also essential to lower carrier concentrations. The electrical properties leveled out at a VI/V ratio between 40 and 100. For the normal MOCVD process, though, the carrier concentration reached its minimum for values of $\sim 4 \times 10^{19}$ cm$^{-3}$, higher than what was achieved with HPCVD. The mobility was also significantly lower than what was obtained by HPCVD, about 180 cm$^2$V$^{-1}$s$^{-1}$.

In order to lower the growth rate and further increase the effective VI/V ratio, pulsed growth was employed. This involved turning the TMBi source on and off every 10 seconds. This was able to significantly improve the electrical properties for films grown by this pulsed method compared to those of similar thickness grown by the normal MOVCD method. For a pulsed-grown film 43 nm thick, the carrier concentration was $2.2 \times 10^{19}$ cm$^{-3}$ and the mobility was 263 cm$^2$V$^{-1}$s$^{-1}$. For a 47 nm thick normally-grown film, the carrier concentration was $3.8 \times 10^{19}$ cm$^{-3}$ and the mobility was 183 cm$^2$V$^{-1}$s$^{-1}$.

X-ray diffraction data of MOCVD-grown films generally showed a broad low intensity peak overlapping with a sharp, strong peak in rocking curve scans. HPCVD-grown films generally only contained a single sharp peak. It was determined that this may be caused by selenium coating the substrate as it heats up before deposition of Bi$_2$Se$_3$ begins. In order to test this, an MOCVD growth was performed in which the DMSe source was turned on while the susceptor heated up and before the TMBi was turned on. This growth resulted in a rocking curve with a single sharp peak, much like
what is usually seen for HPCVD growth. Thus it seems that having a thin selenium layer on the sapphire substrate helps produce immediate high quality epitaxial growth rather than having a more disordered initial layer as evidenced by the broad and sharp overlapping peaks usually seen for MOCVD growth. Exposing the substrate to selenium also improved the carrier concentration, dropping it to $1.1 \times 10^{19}$ cm$^{-3}$ versus $3.8 \times 10^{19}$ cm$^{-3}$ for a normally grown MOCVD sample.

**7.1.3 Effects of Ambient Environment**

The study of the effects of different ambient environments on the electrical properties of Bi$_2$Se$_3$ showed that water vapor plays a major role in the oxidation of Bi$_2$Se$_3$ over time. Samples held in both air and water vapor showed up to a 30% increase in carrier concentration over 30 hours and also a large decrease in mobility. Water vapor causes oxidation or hydroxidation of the Bi$_2$Se$_3$ surface, leading to an increase in carrier concentration. Samples held in nitrogen did not result in an increase in carrier concentration for periods up to 30 hours. Samples held in oxygen showed a 20% decrease in carrier concentration over 1-2 hours, then an increase of 20% over the initial value over 30 hours. It is suggested that oxygen molecules act as p-type dopants before reacting to form an oxide, leading to an increase in carrier concentration over time. Water vapor in particular reacts with the Bi$_2$Se$_3$ surface, resulting in free electrons which increase the carrier concentration. These results were confirmed by XPS.
7.2 Future Work

7.2.1 HPCVD

There are methods that have been used to improve the structural and electrical properties of MBE-grown films that could be applied to HPCVD growth of Bi$_2$Se$_3$ also. A two temperature growth method has been shown to improve film quality in MBE growth. Growing a thin layer of several quintuple layers at a low temperature (100-120°C) followed by the remainder of the growth at a more typical temperature (190-250°C) has ensured well-ordered epitaxial growth. They may serve a similar role to selenium coating the substrate at the susceptor heats that is present in our HPCVD growth. Lowering the growth rate further may reduce the number of nucleation sites and increase the grain size.

Compensation doping has been used in MBE growth of Bi$_2$Se$_3$ in order to decrease the carrier concentration and even create p-type films. While a variety of dopants have been used, they introduce the problem of increased scattering sites and decreased mobility. Bi$_2$Te$_2$Se and other ternary and quaternary compounds have shown to be more insulating than Bi$_2$Se$_3$. However, due to the various melting points of precursor materials, HPCVD growth of such compounds may prove difficult. Antimony is a dopant which has been shown to lower the carrier concentration without significantly increasing scattering. Trimethlyantimony (TMSb) and dimethyltelluride (DMTe) are commercially available and could be used as metal organic sources for introducing Te and Sb into the Bi$_2$Se$_3$ lattice.
7.2.2 MOCVD

The most important improvement in MOCVD growth of Bi$_2$Se$_3$ would be to improve the quality of deposition on MgB$_2$. While we were able to achieve deposition of the correct phase of Bi$_2$Se$_3$ onto MgB$_2$, the structural quality was rather poor compared to growth on sapphire. This is likely due to effects from the MgB$_2$ surface. Since MgB$_2$ is not a material with van der Waals bonding, if dangling bonds are present on the surface, it may inhibit type II van der Waals epitaxy growth. These dangling bonds may cause the nucleation of Bi$_2$Se$_3$ planes other than the desired (003) family of planes. As was seen in growth on sapphire, the nucleation of other planes can cause an increase in carrier concentration and decrease in mobility.

It would be useful to optimize the MOCVD growth conditions for deposition on MgB$_2$ further. Since a susceptor normally used for MgB$_2$ growth is used for Bi$_2$Se$_3$ growth, the heating profile and substrate position may be slightly different than was used to optimize MOCVD growth previously. So, varying the substrate temperature and susceptor position may allow results closer to those of Bi$_2$Se$_3$ grown on sapphire.

However, optimizing the conditions may not be enough if dangling bonds on the surface of MgB$_2$ is the real issue. Therefore, passivating the surface of MgB$_2$ could prove essential for high quality growth of of Bi$_2$Se$_3$ on MgB$_2$. Passivation with selenium has been shown to improve the quality of van der Waals epitaxy-grown materials.\textsuperscript{6} Studying how to properly passivate the MgB$_2$ surface with selenium should be rather easy by varying the temperature and time during which the DMSe precursor is introduced to the substrate.
Performing electrical measurements to determine the quality of Bi$_2$Se$_3$ deposited on MgB$_2$ will be essential but more complicated than usual due to the bilayer structure with MgB$_2$. Then determining whether proximity effect-induced superconductivity is present in the Bi$_2$Se$_3$ film and testing to determine the presence of Majorana fermions can be performed.

7.2.3 Oxidation

While nitrogen has been shown to prevent the degradation of the film surface seen in water vapor and air environments, the effects of a vacuum were not studied in depth due to the system setup. While no reactions should take place with a vacuum environment, a high vacuum may cause increased selenium out-gassing, resulting in a higher selenium vacancy concentration and thus a higher carrier concentration. Being able to do Hall measurements over time in a vacuum environment would allow us to determine if this is the case.

Purging the system with nitrogen before pumping to vacuum could also help decrease the water vapor concentration at lower vacuums. Evidence of this was seen when shipping samples with a low vacuum seal with and without being previously purged with nitrogen. The samples that had been purged with nitrogen showed less degradation of the surface after shipping than samples which had not.

A capping layer of selenium on the top of Bi$_2$Se$_3$ films has been shown to minimize the doping effect from air. A study of a sample with such a layer in air compared to an uncapped sample would be good for measuring its effectiveness compared to nitrogen.
7.3 References


Appendix A

Absolute Values for Hall Measurement Oxidation Data

The following graphs (Figure A-1) show the absolute values for data that was given as a percent change over time in Figure 6-2 in section 6.3.1.3. The initial, minimum, and maximum values for this data are also included in chart A-1.

Figure A-1. (a) carrier concentration and (b) mobility for samples held in air, nitrogen, water vapor, and oxygen over time.

<table>
<thead>
<tr>
<th>Property</th>
<th>Air</th>
<th>Nitrogen</th>
<th>Water Vapor</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial CC (cm$^3$)</td>
<td>7.48x10$^{18}$</td>
<td>7.37x10$^{18}$</td>
<td>1.35x10$^{19}$</td>
<td>1.19x10$^{19}$</td>
</tr>
<tr>
<td>Min. CC (1-2 hours) (cm$^3$)</td>
<td>7.12x10$^{18}$</td>
<td>6.70x10$^{18}$</td>
<td>1.24x10$^{19}$</td>
<td>9.3x10$^{18}$</td>
</tr>
<tr>
<td>Max. CC (10-30 h) (cm$^3$)</td>
<td>9.57x10$^{18}$</td>
<td>6.89x10$^{18}$</td>
<td>1.77x10$^{19}$</td>
<td>1.35x10$^{19}$</td>
</tr>
<tr>
<td>Initial Mobility (cm$^2$V$^{-1}$s$^{-1}$)</td>
<td>447</td>
<td>461</td>
<td>324</td>
<td>294</td>
</tr>
<tr>
<td>Mobility (1-2 h) (cm$^2$V$^{-1}$s$^{-1}$)</td>
<td>444</td>
<td>493</td>
<td>318</td>
<td>291</td>
</tr>
<tr>
<td>Mobility (10-30h) (cm$^2$V$^{-1}$s$^{-1}$)</td>
<td>378</td>
<td>488</td>
<td>275</td>
<td>259</td>
</tr>
</tbody>
</table>
Appendix B
HPCVD Growth Conditions for MgB$_2$

The process for the HPCVD growth of MgB$_2$ is similar to that of Bi$_2$Se$_3$. Magnesium pellets are placed in a ring around the substrate, heated to the desired temperature, and then B$_2$H$_6$ is flowed into the chamber, decomposes, and reacts with the magnesium to deposit MgB$_2$ on the substrate surface. The growth process is summarized as follows:

1. Clean Mg pellets in 10% HCl, then rinse in isopropanol
2. Load pellets and SiC substrate onto susceptor
3. Pump reactor to $6 \times 10^{-3}$ Torr
4. Purge with 1200 sccm H$_2$ for 10 min
5. Set pressure to 70 Torr and heat to 720°C
6. Start flow of B$_2$H$_6$
7. Grow for 10 min
8. Turn off B$_2$H$_6$ and keep temp for an additional 20 seconds
9. Turn off heater and wait until susceptor is at 120°C
10. Turn off H$_2$ and pump chamber down
11. Purge the reactor with N$_2$ several times before venting to atmosphere and opening

Table B-1. Growth Conditions for HPCVD Growth of MgB$_2$

<table>
<thead>
<tr>
<th>Magnesium Source</th>
<th>Kurt Lesker Mg pellets (99.95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron Source</td>
<td>5% B$_2$H$_6$ in H$_2$</td>
</tr>
<tr>
<td>Growth Pressure</td>
<td>70 Torr</td>
</tr>
<tr>
<td>Growth Temperature</td>
<td>720°C</td>
</tr>
<tr>
<td>Substrate</td>
<td>SiC</td>
</tr>
<tr>
<td>Growth Time</td>
<td>1 min</td>
</tr>
</tbody>
</table>
VITA

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