Tuning Topological Surface States by Charge Transfer

Zhiyi Chen

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Tuning Topological Surface States by Charge Transfer

by

Zhiyi Chen

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

2016
This manuscript has been read and accepted for the Graduate Faculty in Physics in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract

Tuning Topological Surface States by Charge Transfer

by

Zhiyi Chen

Thesis Advisor: Professor Lia Krusin-Elbaum

Three-dimensional (3D) topological insulators (TI s), Bi$_2$Se$_3$, Bi$_2$Te$_3$, Sb$_2$Te$_3$, are a class of materials that has non-trivial bulk band structure and metallic surface states. Access to charge transport through Dirac surface states in TI s can be challenging due to their intermixing with bulk states or non-topological two-dimensional electron gas quantum well states caused by bending of electronic bands near the surface. The band bending arises via charge transfer from surface adatoms or interfaces and, therefore, the choice of layers abutting topological surfaces is critical. Surfaces of these 3D TI s have also been proposed to host new quantum phases at the interfaces with other types of materials, provided that the topological properties of interfacial regions remain unperturbed.

This thesis presents a systematic experimental study of both bulk conducting and surface charge transfer problems. We started with optimizing growth condition of Bi$_2$Se$_3$ on various substrates, to achieve best quality of Bi$_2$Se$_3$ single layers we can get. We then move on to growth of Bi$_2$Se$_3$/Zn$_x$Cd$_{1-x}$Se bilayers. Here we improved lattice mismatch between Bi$_2$Se$_3$ and Zn$_x$Cd$_{1-x}$Se layers by tuning lattice parameter of Zn$_x$Cd$_{1-x}$Se. After that, we achieved molecular beam epitaxial growth of Bi$_2$Se$_3$/Zn$_x$Cd$_{1-x}$Se superlattices that hold only one topological surface channel per TI layer. The topological nature of conducting channels is supported by $\pi$-Berry phase evident from observed Shubnikov de Haas quantum oscillations and by the associated two-dimensional weak antilocalization quantum interference correction to magnetoresistance. Both density functional theory calculations and transport measure-
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The first chapter contains a brief introduction to TIs. It describes basic concepts and notations used later in the bulk of the thesis. These include the topological surface states of a TI, crystal structure of 3D TIs, the origin of defects and their effects on transport study.

The second chapter presents experimental techniques employed for growth and for structural, and electrical characterization of the 3D TIs thin films and superlattices. First, every component of our custom-designed molecular beam epitaxy system will be described in detail, and then the important in situ surface morphology monitoring tool — RHEED will also be mentioned, as well as high resolution X-ray diffraction (XRD). In the second part, a standard procedure for device fabrication will be presented. The last part will focus on the electron transport measurement setup and various techniques for characterization.

In the third chapter we present explorations of different substrates for growth of Bi$_2$Se$_3$ thin films, describe growth of Bi$_2$Se$_3$ thin films on sapphire, GaAs(111), InP(001) and InP(111), then optimize growth conditions accordingly. The quality of films are investigated to study the effects of substrates on quality of the films.

The fourth chapter is a growth study of superlattice of a TI with a traditional II-VI semiconductor, Bi$_2$Se$_3$/Zn$_x$Cd$_{1-x}$Se. we explore II-VI semiconductor family and study the optimal material to grow on top of Bi$_2$Se$_3$. Then we focus on the growth of Bi$_2$Se$_3$/Zn$_x$Cd$_{1-x}$Se superlattice and structural study.

The fifth chapter studies charge transfer at the interface between Bi$_2$Se$_3$ layer and Zn$_x$Cd$_{1-x}$Se layer. We start by looking at the result of charge transport study of our superlattice. Then we will present the result of our density functional theory (DFT) calculation, which showed completely different charge transfer between Bi$_2$Se$_3$ sits on top of Zn$_x$Cd$_{1-x}$Se and Zn$_x$Cd$_{1-x}$Se on top of Bi$_2$Se$_3$. This will provide a perfect explanation of our experimental results. Then we designed experiment using transport measurement to test
and confirm our explanation.

The sixth chapter gives a short summary of this thesis work and a proposal for future work.
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I would like to thank Professor Lia Krusin-Elbaum first and foremost, for her valuable guidance and support over the years. The enthusiasm and perseverance she has for her research was contagious and motivational for me. Her intuitive insight of scientific research guided me through the research process and helped me develop feasible ideas. Lia has been a role model scientist, a dear friend, and most importantly, a great mentor. I cannot express how much gratitude I owe her.

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1.1 Introduction to Topological Insulators

The constant theme of condensed matter physics is to discover and classify distinctive states of matter. Using Landau’s approach, which describes phases of matter in terms of the underlying symmetries that are spontaneously broken, one can classify crystalline solids, magnets and superconductors by broken translational, rotational and gauge symmetries, respectively. The discovery of the quantum Hall state in 1980 [9], provided the first example a different classification, based on the notion of topological order [10, 11]. This new quantum state that has no spontaneous symmetry breaking, but it belongs to a topologically ordered...
phase that is unique from other states of matter: its properties are insensitive to smooth changes in materials and would not change unless there is a quantum phase transition.

Since 2005, a new quantum state of matter called topological insulators (TIs) emerged in condensed matter physics. It started with theoretical predictions [12, 13, 14] and was soon confirmed by experimental observations [15] in real materials. Similar to quantum Hall state, TIs have topological surface states which are protected by a topological order. This makes TIs topologically distinct from all previously known states of matter.

Like ordinary insulators, TIs have a bulk bandgap which separates the conduction band and the valence band. However, the surface of TIs has gapless electronic states that are protected by symmetry. Those unique surface states provide a playground for discovering exotic physics such as QAHE [16, 17], Majorana fermion [18] and magnetic monopoles [19]. In addition to hosting such novel states and particles, these surfaces states are predicted for a wide range of potential applications from spintronics to quantum computation.

1.1.1 Topology 101

It is essential to give a brief introduction of topology before we move on, so we will be able to see the connection between physics and topology.

The key topology concept here is "smooth deformation", which means a continuous change in shape without creating holes. Any shape that has same amount of holes belongs to a same class. One shape can be smoothly deformed into another if they are both in the same topological class. For example, Figure 1.1 shows a dumbbell and a basketball on the top, and they are in the same topological class because they both have no hole, while the weight plate and the kettlebell belong to another topological class, as they both have one hole. Those two classes can not be deformed smoothly between each other without opening or closing a hole, while in those classes one can be deformed smoothly into another.

1.1.2 Electronic states of topological insulators

Let us start with the most basic electronic state of matter – insulator. As shown in Figure 1.2(a), electrons are localized to the atoms, hence have zero contribution to conductance. In
Figure 1.1: Topological classes. The dumbbell and basketball on the top is topologically distinct from the weight plate or the kettlebell at the bottom because they cannot be smoothly deformed to another class without creating a hole. Similarly, ordinary insulators and topological insulators belong to different topological classes.
the language of band theory, a insulating state can be described using a bandgap between the occupied valence band states and the empty conduction band states. Topology classification can be used to classify quantum states, using bandgap to mimic holes. Therefore, ordinary insulators and intrinsic semiconductors belong to the same topological class, which has an energy gap. We can call them topological equivalent as there exists an adiabatic path connecting the energy structures of the two, along which the energy gap remains finite (non-zero).

As we discussed earlier, quantum Hall state is a new class of topological order, which occurs when electrons are confined in two dimensions under a strong magnetic field. Lorentz force drives electrons to move in circular motion, as shown in Figure 1.2(b). This circular motion looks like the electrons in the previous case, but the electrons are not bounded to atoms here, and the driving force is Lorentz force. Quantized orbitals and quantized energies are formed, $E_n=\hbar \omega_c (n+1/2)$, where $\omega_c$ is cyclotron frequency. Discrete energy states lead to an energy gap separate occupied states and unoccupied states, just like an ordinary insulator. However, at the edge, the circular orbits will bounce off the edges of the system leads to the so-called "skipping orbits", as shown in Figure 1.2(b). These skipping orbits only allow electron motion in one direction and do not have quantized energies, hence they can conduct. These states are also know as "edge states". These edge states are perfect for electrical transport. Because there are no backward-moving modes available, electrons would not bounce off non-magnetic impurities as they normally do. This leads to this "dissipationless" transport, which will not suffer from energy loss such as heat.

Now let us switch to 2D topological insulator. Strong spin-orbit coupling replace the role of strong magnetic field in the quantum Hall state case, hence topological insulators occur in the absence of a magnetic field. As shown in Figure 1.2(c), spin-up and spin-down states are each in quantum hall states. The spin of electrons is locked to the direction of propagation due to strong spin-orbit coupling. There is again an energy gap forming and edge states conducting on the edge. Since there are states propagate in both directions, time-reversal symmetry plays a fundamental role here. Mathematically, time reversal symmetry means that if we choose to parametrize time in the system by $-t$ instead of $t$, then the
Figure 1.2: (a) The insulating state is characterized by an energy gap separating the occupied and empty electronic states, which is a consequence of the quantization of the energy of atomic orbitals. (b) In the quantum Hall effect, the circular motion of electrons in a magnetic field, \( B \), is interrupted by the sample boundary. At the edge, electrons execute "skipping orbits" as shown, ultimately leading to perfect conduction in one direction along the edge. (c) The edge of the "quantum spin Hall effect state" or 2D topological insulator contains left-moving and right-moving modes that have opposite spin and are related by time-reversal symmetry. This edge can also be viewed as half of a quantum wire, which would have spin-up and spin-down electrons propagating in both directions. (d) The surface of a 3D topological insulator supports electronic motion in any direction along the surface, but the direction of the motion uniquely determines its spin direction and vice versa. The 2D energy—momentum relation has a "Dirac cone" structure similar to that in graphene.

From reference [1]
Hamiltonian will remain unchanged. For example, a quantum spin Hall insulator preserves time-reversal symmetry (opposite spins have opposite chiralities). Time reversal switches both the direction of spin and the direction of momentum, interchanging the two counter-propagating modes. On the other hand, quantum Hall states breaks time-reversal symmetry.

3D topological insulator presents a more complicated picture, as will be explained in more details in the next section. Nonetheless, the surface states of a 3D topological insulator resemble the edge states of a 2D topological insulator. As in the 2D case, in a 3D topological insulator the direction of spin is perpendicular to the direction of electron propagation on the surface, as shown in Figure 1.2(d). Also as in the 2D case, back-scattering is forbidden for the surface states of a 3D topological insulator, which is guaranteed by time reversal symmetry. For an electron to be back scattered, there has to exist a state which has its opposite momentum, while spin direction and everything else stays the same. That state does is not available, thanks to time reversal symmetry. Hence, the surface states of topological insulators are topologically protected against backscattering. Using the language of topology, metals, quantum Hall effect, 2D and 3D topological insulators belong to other topological classes due to the absence of an energy gap. The process of an ordinary insulator changing to a topological insulator is a phase transition, which involves the closing of bandgap. This is the origin of the term ‘topological protection’. Several articles [20, 21] review these concepts in detail.

1.2 3D Topological Insulators and surface states

The materials we are focusing on in this thesis are the second generation three dimensional topological insulators, Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$. It started with the predictions based on first-principle calculations [2], which predicts these materials should have a bulk bandgap and a single Dirac cone on the surface. These predictions were soon confirmed by experimental observations in angle-resolved photoemission spectroscopy (ARPES) [3, 4, 22] and scanning tunneling microscopy (STM) [23, 24, 25] measurements. The theoretical calculation and ARPES measurements results of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ are shown in Figure 1.3. The broad
1 Introduction

1.2 3D Topological Insulators and surface states

Figure 1.3: (a) and (c) Energy band structures of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ on (0001) surface respectively. Local density of states (LDOS) are indicated by the color—warmer colors indicates higher LDOS. Red regions indicate bulk energy bands while blue regions indicate bulk energy gaps. The surfaces states are indicated by red linear lines crossing the $\gamma$ point. From reference [2]. (b) and (d) ARPES measurements of band dispersions [3, 4].
bulk band (bulk conduction band and bulk valence band) dispersions are similar to those in (a) and (c), whereas the sharp V-shape dispersion is from the surface state. The V-shape dispersion cross at Dirac point. Note that Dirac points are lower than fermi level in both Bi$_2$Se$_3$ and Bi$_2$Te$_3$ shown in Figure 1.3, which means they are n-type. We will get to that in the next chapter. Another thing we should notice, is that Bi$_2$Se$_3$ has a larger bulk band gap than Bi$_2$Te$_3$ (Sb$_2$Te$_3$ as well). And unlike Bi$_2$Te$_3$ or Sb$_2$Te$_3$, the Dirac point is not wrapped by bulk states in Bi$_2$Se$_3$. Both these features make Bi$_2$Se$_3$ the most studied candidate for the transport studies, as it is easier to separating surface contribution from that of the bulk. Hence, or the rest of this thesis we will focus on Bi$_2$Se$_3$.

1.3 Crystal structure and defects

Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ share the same rhombohedral crystal structure, and all have five atoms per unit cell. Taking Bi$_2$Se$_3$ for example, as show in Figure 1.4, it consists of five-atom layers stacked along the z direction, which is known as quintuple layers. Each atom layer form a hexagonal plane. Each quintuple layer consists of two Bi layers and three Se layers. Between two layers inside a quintuple layer, the coupling is very strong, while two quintuple layers are coupled by van der Waals force in between. Since each QL is about 1 nm thick, the lattice constant along the c-axis is about 3 nm.

As indicated earlier, Bi$_2$Se$_3$ samples are intrinsically n-type. This has become a big obstacle, preventing the surface states from being detected in transport measurements. The reason for this n-type conduction is that the formation energy of Se vacancies is very low as suggested by first-principles pseudopotential calculations, and the existence of Se vacancy on Bi$_2$Se$_3$ has been confirmed by STM measurements [26].

Other than injecting conducting electrons, Se vacancies can also considerably modify the surface band structures. It might sounds counterintuitive at first, as topological surface states are known to be robust against non-magnetic disorders. However, as been demonstrated by STM studies [27], when large numbers of Se vacancies form on the surface, topological surface states move from surface to lower quintuple layer.
Figure 1.4: Crystal structure of Bi$_2$Se$_3$. A quintuple layer is indicated by a red box, which contains three Se layers and two Bi layers.
All these effects make Se vacancies a detriment on our path, and we will explore different ways to eliminate them in the next chapter.

1.4 Charge transfer at the interface

Another materials challenge to accessing topological states in TIs is charge transfer to the surfaces from abutting environments, which induces bulk band-bending and 2DEG quantum well states that lack topological protection and intermix with topological surface states. This is often referred to as ‘ageing effect’. Figure 1.5(a) and (b) are APRES data on Bi$_2$Se$_3$ exfoliated flaked kept in ultra high vacuum ($5 \times 10^{-11}$ torr) and low temperature (6K), showing the downward shift of Dirac cone as respect to time [5]. The near surface reconstruction induce a downward band bending of both conduction and valence bands, forming 2DEG quantum well states, as shown in Figure 1.5(c). This shift the Dirac point of topological surface state further down, as explained in literature [6]. Figure 1.5(a) shows the data for the sample 3 hours after exfoliation, while Figure 1.5(b) shows data for the same sample 34 hours after exfoliation. The charge transfer pushes the Dirac down in the 34 hours sample, making it deeply buried in bulks states. This is our 2nd problem because that also makes the TSS difficult to access.
Introduction

1.4 Charge transfer at the interface

Figure 1.5: Time evolution of the ARPES dispersion of Bi$_2$Se$_3$ at $5 \times 10^{-11}$ torr and $T = 6$ K: (a) 3 hours after cleaving; (b) 34 hours after cleaving [5]. (c) A near-surface electrostatic potential variation causes downward band bending of both the conduction band minimum and valence band edges, forming a surface quantum well. It shifts the Dirac point of the topological surface states (yellow band) further below the Fermi level and causes the conduction band states to be restructured into ladders of Rashba-split two-dimensional subbands, $E_n$ (red bands), with envelope wave functions (dark red) peaked close to the surface. A schematic spin texture of these states is shown by the arrows [6].
The main theme of material science has always been discovering new materials and improving the quality of current materials. Synthesizing high quality materials has proven to be essential for discovering new physics and exploring novel applications. For example, growth of high quality GaAs thin films with ultra high mobility leads to the discovery of quantum Hall effect [9].

As explained in the last chapter, bulk conductivity is a major problem for Bi$_2$Se$_3$ and other 3D TIs. There are different routes we can choose to solve this. Bulk resistivity can be significantly increased using dopants such as Ca or Sb, but the downside is an additional sublattice disorder and possible clustering, both difficult to control [28, 29]. Electrostatic
gating across the bulk bandgap in device structures based on TI thin films and crystalline flakes [30, 31, 32] have been more promising, although surface oxidization and surface contamination can be a problem [33, 34]. One obvious way to decrease the contribution of the bulk is by increasing the surface to bulk ratio using nanostructuring which can be carried out through mechanical exfoliation, or growth of TI thin films. In this thesis we have chosen the latter, and turned to molecular epitaxy (MBE) to produce high quality thin TI films.

2.1 Molecular beam epitaxy

MBE is the most powerful tool to grow single crystalline epitaxial thin films. It was developed by Arthur and Cho in Late 60s [35, 36], to grow GaAs/InGaAs structure. This technique has been widely used to grow semiconductors, metals, oxides during the past half century.

MBE growth gives us several advantages. First, the growth is in an ultra high vacuum (UHV) chamber. For example, background pressure in the chambers we use is $10^{-10}$ to $10^{-11}$ mBar. The ultra-high vacuum in MBE reduces the incorporation of unwanted impurities, which is key in the exploration of transport properties, and reduces ambiguities when incorporating wanted dopants. Second, the MBE growth utilizes fluxes of constituent elements from Knudsen effusion cells. The molecular beams coming out of Knudsen cells impinge on a heated substrate, forming an epitaxial growth. The growth process is very slow, which gives us highly ordered materials. The ability to tune fluxes from individual element sources also give us better control of composition, thickness, crystalline and interfacial quality. Third, the technique gives us access to a variety of materials, allowing us to perform heterostructure growth and modulation doping.

2.1.1 System overview

The system we used is a three-chamber Riber 2300P system; it is shown in Figure 2.1. The left chamber is dedicated to the growth of III-VI materials. The chamber contains In, Ga, As(X2), Al, Mn, Be and Si sources. The middle chamber is dedicated to II-VI materials growth; this chamber is loaded with Zn(X2), Cd, Mg, Se, Te, N, ZnCl$_2$ and Bi. On the right
2 Experimental methods

2.1 Molecular beam epitaxy

Figure 2.1: Drawing of the Riber 2300P system in our lab.

side, there is a metallization chamber, which has been modified for the dedicated growth of TI. All these three chambers are connected through a UHV transfer channel, facilitating shuttling of samples between different chambers without breaking vacuum.

Figure 2.2 shows a picture of the TI chamber after modification. From bottom to top, we have a CTI-7 cryo pump, which gives us $10^{-10}$ mBar background pressure. Then there are Bi and Se Knudsen cell which provide molecular beams for Bi and Se. We have recently replaced the Bi cell by a new double source cell, allowing us to have access to an additional molecular beam in this chamber. Slightly above the cells, there is a four-ports e-beam evaporator, which gives us access to other materials such as Cr and Nb. Above the e-beam evaporator, we have an electron gun for reflection high energy electron diffraction (RHEED), which is used to monitor the growth in situ. RHEED is a very important tool for the MBE growth, and will be described in the next subsection. Above the RHEED gun, we have the substrate heater. Then there are two flux gauges on the top, monitoring the pressure in the chamber and the flux shooting at the substrate respectively.
2 Experimental methods

2.1 Molecular beam epitaxy

Figure 2.2: A picture of the TI chamber after modification. Important parts are indicated by red arrow and labeled.
2.1.2 Reflection high energy electron diffraction

RHEED is a widely used technique to monitor substrate preparation and film growth in real time. The RHEED system in our chamber is a RH-15 system from Staib instruments. The electron gun generates electrons at 15 KeV, aiming at the substrate at a grazing incidence. The diffraction pattern is projected to a phosphor screen. The incident angle is typically 3 to 5 degree, which means the penetration depth of electrons of nanometer scale. Hence, RHEED probes the top surface of the sample.

Just like other diffraction techniques, it can be understood following Ewald sphere and Laue conditions. Constructive interference occurs when the Ewald sphere intersects with the reciprocal lattice rods, resulting in a RHEED pattern. So the streaky RHEED patterns indicate smooth surfaces on the sample. On the other hand, spotty pattern indicates that the sample has a rough surface. For example, Figure 2.3(a) shows the surface of a Bi$_2$Se$_3$ surface with streaky lines, indicating a smooth surface.

RHEED can also be used to probe surface reconstruction at the surface of a sample. The surface atoms of material rearrange themselves in a different way from the bulk atoms, because there is no bonding on the vacuum side. A famous example is the 7 X 7 reconstruction on Si(111) surface. The reconstruction we encounter most frequently is the (2 X 4) reconstruction which happens at GaAs(001) surface. Here, 2 means the spacing between surface atoms is twice as the spacing between bulk atoms in one direction ([110] in this case), while 4 means the spacing between surface atoms is four times as the spacing between bulk atoms in perpendicular direction. In reciprocal space, it will show up as lines which has 1/2 and 1/4 spacing respectively. Figure 2.3(b) shows the 2X pattern on GaAs(001) surface.

Another useful information we get is the symmetry of the surface. When we rotate the sample in plane while monitoring RHEED patterns, we can observe the pattern repeats several times in one rotation. For example, at Bi$_2$Se$_3$ surface, we see the pattern repeating every 60 degrees, consistent with the six fold symmetry.
Figure 2.3: RHEED image showing streak lines for Bi$_2$Se$_3$ indicating a smooth surface (left) and 2X pattern for GaAs(001) surface (right).
2.2 Structural characterization

Post growth, various techniques were employed to investigate structure properties of the material. The techniques we used mostly were X-ray diffraction (XRD) and atomic force microscopy (AFM). These characterization methods allowed us to evaluate sample quality and provided us with feedback needed to optimize film growth.

2.2.1 X-ray diffraction

X-ray diffraction (XRD) is the most important tool in characterizing the structure of materials. It is the first measurement we perform after we take the sample out of MBE chamber and check under microscope. The information it gives us includes crystal structure, preferred orientation, lattice parameters, film composition and stress, as shown in Figure 1.4(a).

The XRD equipment we have is a Bruker D8 Discover, equipped with a high resolution detector and a two dimensional detector. This allows us to construct pole Figures and gives us information in both $\gamma$ and $2\theta$, as shown in Figure 2.4(b) and (c).

2.2.2 Atomic force microscopy

Atomic force microscopy is a scanning probe microscopy with nano scale resolution. It comprises a cantilever with nano-sized semiconducting tip. The cantilever can vary from 10 to 500 micrometers in size, and is usually made of Si or SiN. During measurement, the tip on the cantilever feels the force from the sample. The resulting deflection of the cantilever is illuminated by a laser beam and then detected by photodiode array.

AFM can work in contact and non-contact modes. In the contact mode, the tip is very close to the sample. In the non-contact mode, the tip is several nanometers away from the sample, as van der Waals force is strongest in that region. The tip is vibrating at a frequency slightly higher than its resonant frequency. The feedback signal gives the distance between sample and tip, which allows the scanning software to reconstruct topography of the sample. An example scan is shown in Figure 1.5.
Figure 2.4: (a) An example of XRD $2\theta$ scan. (b) and (c) Pole Figures of Bi$_2$Se$_3$ on two different planes.
2 Experimental methods

2.3 Device fabrication

After the samples are taken out of MBE chamber, they are prepared for transport measurement.

When lithography is not required samples are cut into small squares (slight smaller than 3 mm x 3 mm for small chip carrier, 6 mm x 6 mm for large chip carriers). Gold is then deposited on four corners of the sample through a shadow mask. Then silver epoxy (sometimes wire bonder) is used for bonding gold wires to the sample and an appropriate chip carrier.

To pattern the Bi$_2$Te$_3$ films into specific shapes required for transport measurements we have developed two specific wet etch recipes.

In one we used hydrobromic acid with the following recipe: 0.21 g potassium dichromate (K$_2$Cr$_2$O$_7$) powder, 17 mL hydrobromic acid (HBr), and 50 mL DI water. It gives an etching rate of 1 nanometer/second and it leaves a very smooth surface. This recipe has been used for patterns as small as 3 micrometers.

Second recipe using aqua regia was mostly used for etching Sb$_2$Te$_3$. The etchant mixture used was 16% HNO$_3$, 8% HCl, and 76% DI water. It gives an etching rate of about 3 nanometer/second depends on the quality of Sb$_2$Te$_3$ film. This recipe has been used for
patterns as small as 20 micrometers.

2.4 Electrical transport measurement

Transport measurements were performed mainly in Quantum Design Physical Property Measurement System (PPMS), which is equipped with a 14 Tesla superconducting magnet and has a temperature range from 1.9 K to 400 K. We also have a modified Quantum Design Magnetic Property Measurement System (MPMS), which is equipped with a 5 Tesla superconducting magnet and has a temperature range from 1.9 K to 400 K. Since the MPMS was not originally designed for transport measurements, we designed an external measurement setup. PPMS comes with a Model 6000 source-measurement units capable for three sets of four-terminal resistivity measurements. However, it is not suitable for our samples configured with van der Pauw contact layout. As it was, the PPMS system could not handle very high resistance samples. To accommodate such samples we built an external measurement setup expanding the range of both MPMS and PPMS instruments. In the reconfigured system Keithley 6221 was used as both DC and AC current source. Keithley 2002 was used for the voltage measurements when sample resistance was far less than 10 MΩ. HP 34401A was used as a backup voltage measurement. Because it has two options for its internal impedance, 100 MΩ and 10 GΩ, it is capable to measure samples of resistance smaller 1 GΩ. For low resistance samples, the voltage signal can be very small and the signal-to-noise ratio is not satisfactory in DC measurements, in which case AC transport measurements were preferred. Keithley 6221 provided AC current ranging from 2 pA to 100 mA at frequencies up to 100 kHz. We used Signal Recovery 5210 lock-in amplifier with analog demodulators; it has an excellent signal-to-noise ratio, and is widely referenced as the benchmark lock-in amplifier. Keithley 228A voltage/current source was used as a source for gating voltage. It can provide voltage ranging from -100 V to 100 V.
Growth of high quality Bi$_2$Se$_3$ films is not only crucial to the fundamental studies of topological insulators (TIs), but also key to making them technologically relevant. In this chapter, we describe our work on the hetero-epitaxy of single crystal Bi$_2$Se$_3$ thin films on GaAs and InP substrates by molecular beam epitaxy (MBE). Surface topography, crystal structures and electrical transport properties of the highly c-axis oriented Bi$_2$Se$_3$ epitaxial films with atomically sharp interfaces are presented.
Figure 3.1: Lattice constants and energy gaps of different substrates and TI materials. Various substrates are marked by open symbols, while TI materials are marked by solid squares. Clearly, some alloys of III-V or II-VI semiconductors can be used as lattice-matched substrates for the growth of TI materials. The table at the bottom lists lattice mismatch of different substrates. From reference [7].


\section{Substrate considerations}

Since we are growing epitaxial layers the choice of substrate may be important, and may impact materials properties such as interface flatness and sample crystallinity. As explained in the first chapter, we have a multiple chamber MBE system with III-V and II-VI chambers, which allows sophisticated substrate preparations.

Prior to this work, MBE films of Bi$_2$Se$_3$ have been grown on substrates like graphene/SiC \cite{37, 38}, silicon \cite{39, 40, 41, 42}, SrTiO$_3$ \cite{43, 44}, GaAs \cite{45, 46}, sapphire \cite{47} and so on. In this study, we investigate Bi$_2$Se$_3$ growth on Sapphire(001), GaAs(111)B, InP(001) and InP(111)B. GaAs and InP are two very commonly used III-V semiconductors. Improving sample quality on these two substrates will not only pave the way to further studies and spintronics applications on these substrates, but also make the whole III-V semiconductors family available for growth of superlattice and heterostructures with Bi$_2$Se$_3$ for device applications.

For traditional epitaxial growth, lattice mismatch is a key parameter. However, for 3D TIs, the existence of van der Waals bonds between quintuple layers make the growth mechanisms different. As our study will show, lattice match becomes a less strict parameter. Although films of best structural quality are achieved on most matched substrates, decent quality epitaxial films can still be grown on a variety of substrates with a large mismatch.

Figure 3.1 shows lattice constants and energy gaps for some of the most widely used semiconductors. This plot contains the data used in choosing the substrate or designing a heterostructure. From the dotted line drawn for Bi$_2$Se$_3$, we can see that it is best matched to CdS and InP. Although ZnSe and CdSe seem relatively far from the line (they are on two different sides of the line), the alloy Zn$_x$Cd$_{1-x}$Se can be grown to be lattice matched to Bi$_2$Se$_3$ if stoichiometry is carefully tuned.

\section{Experimental procedure}

Our Bi$_2$Se$_3$ thin films were grown in a dedicated growth chamber which is connected by UHV transfer modules to two other chambers, one for the growth of II-VI compound semi-
conductor structures and the other for III-Vs, so that seamless transfers between chambers can be accomplished, both for use of the diagnostics tools installed in those chambers, such as RHEED, and for growth of multilayered structures combining TIs with conventional semiconductors or metals. The TI chamber is pumped by means of a cryopump and a small ion pump, and typically exhibits a vacuum level of less than $1 \times 10^{-9}$ Torr during growth. High purity 6N Bismuth (Bi) and Selenium (Se) fluxes were provided by conventional Knudsen cells and measured by Ion gauges placed in the path of the fluxes. We found that an optimal beam equivalent pressure ratio of $\sim$1:10 Bi to Se [48] leads to growth rates of 30 nm/h as confirmed by ex situ film thickness measurement. A lower Bi flux leads to slower growth rates, and higher Bi flux to diminished material quality. Substrate temperature during MBE growth was calibrated to a nominal temperature of 200°C. This condition was optimal; higher temperatures produced reduced growth rate or no growth at all while lower temperatures have led to a diminished material quality. Samples were investigated with reflection high energy electron diffraction (RHEED) immediately after growth. X-ray diffraction (XRD), atomic force microscopy (AFM), cross-sectional high resolution transmission electron microscopy (HRTEM) and Raman spectroscopy were carried out after the sample was taken out of the chamber. Transport measurements were carried out in a Physical Property Measuring System (PPMS).

### 3.3 Results and discussion

#### 3.3.1 Bi$_2$Se$_3$ on sapphire

Different substrates and surface preparation procedures were performed on a number of different substrates. For Bi$_2$Se$_3$ grown on GaAs and InP, after a standard procedure of removing the oxide, a III-V buffer layer was grown in a III-V chamber before the growth of Bi$_2$Se$_3$ layer. GaAs was grown on the GaAs substrate and lattice-matched InGaAs was grown on the InP substrate. For the samples grown on InP(001) substrates, a second buffer layer of ZnCdSe, also lattice-matched to InP, was grown on the InGaAs layer in a II-VI chamber, prior to the growth of Bi$_2$Se$_3$, which was done in a third chamber dedicated to
Figure 3.2: (a) RHEED diffraction patterns of Bi$_2$Se$_3$ film on sapphire taken after the film growth. (b) X-ray diffraction of a ~20 nm thick Bi$_2$Se$_3$ film. The (003) family of peaks shows the film is highly c-axis oriented. (c) High resolution XRD showing thickness fringes for the (006) peak. It indicates good crystal quality.
their growth. For Bi$_2$Se$_3$ grown on sapphire, the substrate was heated up to 650°C for 2 hours prior to growth. The GaAs and InP substrates used in this experiment were semi-insulating, while the sapphire was undoped. All substrates had a miscut to their desired plane below $0.5^\circ$.

Sapphire(0001) was first attempted because it is relatively well studied [47], allowing us to verify our own Bi$_2$Se$_3$ growth conditions. Prior to growth, sapphire was degassed at 450°C for 30 minutes, raised to 650°C at a rate of 5°C per minute, then left there for 2 hours. Figure 3.2(a) shows the RHEED pattern of one sample grown at 200 °C with selenium rich growth conditions (Bi/Se flux ratio about 1:10). Sharp $1 \times 1$ diffraction streaks confirm the good crystalline quality of the film. The crystalline order of the sample was also confirmed by the strong signal from the Bi$_2$Se$_3$ layer in XRD, which is shown in Figure 3.2(b). A high resolution XRD 2thita-omega scan of the Bi$_2$Se$_3$ layer 006 peak is shown in Figure 3.2(c), and we can see multiple fringes around the main peak. Those fringes, also know as thinkness fringes, come from the phase difference between bottom and the top surfaces. From the spacing between those size peaks, we can retract the thickness of the film. And seeing these fringes are indication of good crystal quality.

The morphology of the films is shown in Figure 3.3(a) as characterized by AFM, with RMS roughness of $\sim 0.6$nm. These results are comparable to other samples reported in the literature [47], indicating that our growth conditions are optimal. A Raman spectrum from the sample in Figure 3.3(b) shows three characteristic peaks, at 37, 72.5,132 and 173.5 cm$^{-1}$, which correspond to the $E_{1g}$, $A_{1g}$, $E_{2g}$ and $A_{2g}$ vibration modes respectively, as reported for Bi$_2$Se$_3$ single crystal [49]. That indicates we have the appropriate modes at the expected energies for Bi$_2$Se$_3$. Electrical measurements were carried out at $T = 2$ K using van der Pauw contact configuration in magnetic fields up to 5T applied in the direction perpendicular to the film’s plane. Fig. 3.3(c) shows a cusp in the magnetoresistance (MR) measurement consistent with weak anti-localization, as was reported in the literature [50, 51] for Bi$_2$Se$_3$. From the Hall measurements, our sample was found to be n-type.
Figure 3.3: (a) AFM image of the surface of the film. The rms roughness of the film is \( \approx 0.6 \) nm. (b) Raman spectrum of a 20nm film shows four characteristic peaks, which are \( E_g^1 \), \( A_{1g}^1 \), \( E_g^2 \) and \( A_{1g}^2 \) modes of Bi\(_2\)Se\(_3\) single crystal. (c) MR of the sample taken at \( T = 2 \) K.
3 Single layer growth

3.3 Results and discussion

Figure 3.4: (a) An illustration of the structure grown on GaAs(111)B. (b) RHEED image with streaky lines indicating a smooth sample surface. (c) AFM image of the surface of a film. The RMS roughness of the film is $\sim 2.6$ nm.
Figure 3.5: (a) X-ray diffraction of a \(\sim 20\) nm thick \(\text{Bi}_2\text{Se}_3\) film. The (003) family of peaks shows the film is highly \(c\)-axis. (b) Raman spectrum of a 20nm film shows four characteristic peaks. (c) MR of the sample taken at \(T = 2\) K.
3 Single layer growth

3.3 Results and discussion

3.3.2 Bi$_2$Se$_3$ on GaAs(111)B

The main objective of this work was to grow TI films on III-V semiconducting substrates because of their many technological applications. As a widely used technologically important III-V substrate, GaAs(111) surface has a hexagonal lattice with 3.55% lattice mismatch to Bi$_2$Se$_3$, and it has been successfully used with different methods [45, 46]. Figure 3.4(a) shows the structure of our sample on GaAs(111)B, which includes a 150 nm thick GaAs epitaxial buffer layer. In Figure 3.4(b), a streaky RHEED image indicates a smooth sample surface. Figure 3.4(c) shows the sample with smaller triangular features having a lateral size of roughly 100 nm and a few nm in height that grew atop the larger ones. Here, the measured RMS value is about 2.6 nm.

Figure 3.5(a) shows the result of XRD confirming the main peaks. In Figure 3.4(b), Raman result confirms the right phonon modes. Figure 3.4(c) shows weak anti-localization. From the Hall measurements, our sample was found to be $n$-type. The sheet carrier concentration was around $4 \times 10^{13}$ cm$^{-2}$ and the mobility was found to be 520 cm$^2$(V s)$^{-1}$, which is comparable to the samples grown on GaAs by other groups [45].

3.3.3 Bi$_2$Se$_3$ on InP(001)

InP is another important III-V substrate with the same zinc blend lattice structure as GaAs. Bi$_2$Se$_3$ on InP(001) has been successfully grown by MBE to get Bi$_2$Se$_3$(221) [52], and by hot well epitaxy [53] to get (001) orientation. In this case we grew a ZnCdSe buffer to improve the chemical compatibility between the substrate and the TI, based on similar work which used a ZnSe buffer on GaAs(111)B [45]. The structure is shown in Figure 3.6(a). We observed an abrupt transition of the RHEED pattern from $2 \times 1$ of the ZnCdSe surface (Figure 3.6(b)) to a sharp and streaky pattern of the Bi$_2$Se$_3$ surface (Figure 3.6(c)). When we look at the RHEED screen while rotating the sample, we see the features in Figure 3.6(c) repeat every 60 degrees, which suggests our samples have a 6-fold pattern which is characteristic of the Bi$_2$Se$_3$ hexagonal structure. Figure 3.6(d) shows AFM image of the sample surface, which has a RMS roughness of ~0.8 nm.

We also observed a strong signal in XRD from our Bi$_2$Se$_3$ layer as can be seen in Figure...
Figure 3.6: (a) An illustration of the structure grown on InP(001). (b) RHEED image of the sample after growth of ZnCdSe buffer. (c) RHEED image of the sample after growth of Bi$_2$Se$_3$ film. (d) AFM image of the surface of a Bi$_2$Se$_3$ film grown on InP(001). The RMS roughness of this film is $\sim 0.8$ nm.
Figure 3.7: (a) X-ray diffraction of the Bi$_2$Se$_3$ film. (b) Raman spectrum with (XX) and (XY) polarizations, collected from the 20 nm Bi$_2$Se$_3$ film.
Figure 3.8: (a) HRTEM image of the heterostucture showing epitaxial growth Bi$_2$Se$_3$ on ZnCdSe buffer with a clean interface. (b) MR data at different temperatures in a sample grown on InP(001), with the thickness $t = 20$ nm.
3.7(a). In Raman spectroscopy in Figure 3.7(b) we used parallel (XX) and perpendicular (XY) polarization configurations of the incident and scattered light. In the upper curve, the polarizations of the incident and scattered light are parallel to each other. This curve corresponds to the $x-x$ component of the Raman tensors, while the lower curve corresponds to the case two beams are perpendicular to each other and thus represents the $x-y$ component. These results are consistent with the crystal symmetry predicted from group theory [54].

To confirm the epitaxial growth of our Bi$_2$Se$_3$ film, HRTEM was performed on one of the samples grown on the ZnCdSe buffer. Figure 3.8(a) shows the image of the interface between Bi$_2$Se$_3$ and ZnCdSe. It shows a smooth and abrupt interface and good crystalline quality. The surface topography of the samples were also characterized by AFM.

In order to make Hall measurements, and to isolate the highly conducting InGaAs buffer, we doped the InGaAs buffer layer with Beryllium, which makes the buffer layer $p$-type, thus creating a space charge region that isolates the TI layer from the buffer layer. Hall measurement shows that the film is $n$-type, and sheet carrier concentration of the samples are $6 \sim 9 \times 10^{12}$ cm$^{-2}$ with mobility of $490 \sim 750$ cm$^2$(V s)$^{-1}$, comparable to the best reported results of Bi$_2$Se$_3$ MBE samples on any substrate [43, 55]. Figure 3.8(b) shows MR data taken at different temperatures. With increased temperature, first a linear behavior around 30 K is observed, and eventually a conventional quadratic MR is recovered.

### 3.3.4 Bi$_2$Se$_3$ on InP(111)B

The InP(111) surface is interesting because of its very small lattice mismatch ($\sim 0.2\%$) with Bi$_2$Se$_3$ and correct symmetry [56, 57]. The structure of the TI film grown on InP(111)B is shown in Figure 3.9(a). A sharp and streaky RHEED pattern observed at the end of growth indicates good surface quality. Figure 3.9(b) shows streaky RHEED lines. AFM image in Figure 3.9(c) shows the smoothest surface of any substrate we attempted with RMS roughness of $\sim 0.3$ nm without any ZnCdSe buffer layer.

A strong signal from Bi$_2$Se$_3$ in XRD was also observed, which is shown in Figure 3.10(a). Raman spectrum in Figure 3.10(b) shows nice sharp peaks corresponding to four phonon modes of Bi$_2$Se$_3$. 

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Figure 3.9: (a) An illustration of the structure grown on InP(111)B. (b) RHEED image showing streaky lines. (c) AFM image of the surface of a Bi$_2$Se$_3$ film grown on InP(111)B. The RMS roughness of this film is \( \sim 0.3 \) nm.
Figure 3.10: (a) X-ray diffraction of the Bi\(_2\)Se\(_3\) film. (b) Raman spectrum showing four phonon modes corresponding to Bi\(_2\)Se\(_3\).
Figure 3.11: (a) High resolution XRD showing thickness fringes on (006) plane. (b) MR measurement showing weak anti localization.
Figure 3.11(a) shows thickness fringe again for Bi$_2$Se$_3$. We have only seen this on sapphire before, which indicates sapphire and InP(111) are giving us better quality of materials comparing to GaAs(001) and InP(001). Figure 3.11(b) shows weak anti localization from MR measurement.

3.4 Summary

Using III-V and II-VI buffer layers in a multi-chamber MBE system we were able to grow high quality Bi$_2$Se$_3$ epitaxial layers on III-V semiconductor substrates prepared with different surface methods. We obtained good TI quality for GaAs(111)B with GaAs buffer as previously reported [45, 46]. High quality Bi$_2$Se$_3$ on InP(001) was obtained using a ZnCdSe buffer layer, which also exhibited low carrier concentrations and good carrier mobility. The best surface quality film was achieved on InP(111)B substrate, which was grown without a II-VI buffer layer.
In the previous chapter, we discussed how to grow high quality Bi$_2$Se$_3$ thin films on various different substrates. Bi$_2$Se$_3$ based heterostructures are also attracting intense research interest. When Bi$_2$Se$_3$ is proximal to a layer of a conventional superconductor, an exotic topological superconductivity, predicted to host Majorana fermion excitations, is expected to emerge in the interfacial region [58]. Bi$_2$Se$_3$ and ferromagnet hybrid structures can also display novel magneto-transport properties due to the spin-momentum locking [59].

Exotic behaviors arising from topological orders are predicted to be enhanced in structures comprising alternating layers of Bi$_2$Se$_3$ and band insulators [60]. However, due to van der Waals bonding within the layered TI, true heteroepitaxy with three dimensional semi-
conductors is not well understood and must be studied and optimized. And, the question remains whether the subsurface quantum well two dimensional electron gas (2DEG) states of TI bulk origin \[6, 61, 62\] (that can intermix with topological Dirac states) can be controlled with suitable semiconductor barrier layers.

Our aim is to address two main challenges of the Bi\textsubscript{2}Se\textsubscript{3} material. Let me briefly go over those two challenges just to refresh our memory.

One of the challenges in accessing surface states of three-dimensional (3D) topological insulators (TIs) is a significant conductivity in the bulk. Even in Bi\textsubscript{2}Se\textsubscript{3}, which has the largest band gap (\(\sim 0.3\) eV) \[3\] among the family of 2\textsuperscript{nd} generation 3D TIs, electronic transport is dominated by charges donated by selenium vacancies and antisite defects, adding to thermal activation of charge carriers in the bulk. One obvious way to decrease the contribution of the bulk is by increasing the surface to bulk ratio using nanostructuring which can be carried out through mechanical exfoliation, or growth of TI thin films, nanocrystals or nanowires. Growing thin films by MBE is using this strategy. However, large amount of Se vacancies still exist in MBE grown Bi\textsubscript{2}Se\textsubscript{3} films, making the bulk conductive and surface states difficult to detect. By building a superlattice of Bi\textsubscript{2}Se\textsubscript{3} and traditional semiconductor, we have multiple interfaces, hence increase surface to bulk ratio. The anticipated contribution from the surface states should be multiplied and easily accessed in charge transport or in optical measurements \[60, 63\], if the topological properties of the interfaces are preserved.

Another challenge is the interfacial charge transfer from the environment and from the abutting layers.

### 4.1 Growth of bilayers

Regrowth of semiconductors on top of Bi\textsubscript{2}Se\textsubscript{3} is a first step toward growing complex TI/band insulator hybrid structures. The (Zn,Cd,Mg)Se family of II-VI materials was chosen to combine with Bi\textsubscript{2}Se\textsubscript{3} with the expectation that chemical compatibility of selenides will facilitate growth. They have wide band gaps and comparable optimal molecular beam epitaxy (MBE) growth conditions, making them ideal candidates for heterostructures grown by this tech-
nique. Recently Li et al. [63] studied strain effects on interface formation of Bi$_2$Se$_3$/ZnSe grown on Si(111), where the crystalline quality of the ZnSe layer appears not optimal. Here, we grow Zn$_x$Cd$_{1-x}$Se/Bi$_2$Se$_3$ and Zn$_x$Cd$_y$Mg$_{1-x-y}$Se/Bi$_2$Se$_3$ with compositions that yield layers lattice matched to Bi$_2$Se$_3$, hence strain is greatly reduced at the interface and the quality of the material is improved relative to Bi$_2$Se$_3$/ZnSe, as confirmed by high resolution X-ray diffraction (HR-XRD). These ternary and quaternary alloys can be grown with a range of band gaps by changing the composition, while still maintaining lattice-matching conditions. We find that when TI layers in a bilayer structure are sufficiently thin (∼6 nm) the bulk quantum levels can be shifted upwards thus diminishing the undesirable intermixing [64] with Dirac states.

### 4.1.1 Growth procedure

Bilayers of ZnSe/Bi$_2$Se$_3$ (S1), Zn$_x$Cd$_{1-x}$Se/Bi$_2$Se$_3$ (S2) and Zn$_x$Cd$_y$Mg$_{1-x-y}$Se/Bi$_2$Se$_3$ (S3) were grown by MBE on sapphire (0001) substrates. In situ RHEED was used to characterize the samples during the growth. HR-XRD and contactless electro-reflectance (CER), as well as PPMS were used for ex situ characterization.

The growth of Zn$_x$Cd$_{1-x}$Se, Zn$_x$Cd$_y$Mg$_{1-x-y}$Se and ZnSe was conducted in a Riber 2300 MBE chamber with the base pressure ∼8 × 10$^{-11}$ Torr. The Bi$_2$Se$_3$ growth was conducted in a customized vacuum chamber housing in situ RHEED and a flux gauge, with two effusion cells (one for bismuth and one for selenium). The base pressure in this chamber is ∼8 × 10$^{-10}$ Torr. It is connected by ultrahigh vacuum (UHV) transfer modules to the chamber for the growth of the II-VI layers, also with a pressure of ∼8 × 10$^{-10}$ Torr, to avoid contaminants. Prior to growth, the sapphire substrate was degassed at 450°C for 30 min, raised to 650°C at a rate of 5°C per min, then left there for 2 hours. Bi$_2$Se$_3$ was grown at 260°C under selenium rich growth conditions with a Bi to Se flux ratio of about 1:10 and a growth rate of 0.5 nm per min, the conditions we have established previously [65].

The steps used during growth were as follows. First, a thin Bi$_2$Se$_3$ layer was grown on the sapphire substrate and the sample was transferred in vacuum to the II-VI chamber. Next, the growth of the II-VI materials was performed under a Se rich environment, with a flux ratio
Figure 4.1: (a) $(2\theta - \omega)$ scan of the Bi$_2$Se$_3$ layer deposited under a ZnSe layer (S1) show well-defined thickness fringes. (b) Pole figure of the (102) plane of S3 showing six fold symmetry pattern of wurtzite structure.
Figure 4.2: (a), (b) RHEED patterns of the Bi$_2$Se$_3$ layer and Zn$_{0.23}$Cd$_{0.25}$Mg$_{0.52}$Se layer from sample S3 taken along [11\overline20] direction of the Bi$_2$Se$_3$ surface. (c) RHEED pattern from the Zn$_{0.23}$Cd$_{0.25}$Mg$_{0.52}$Se layer (sample S3) along [1\overline10] direction of the Bi$_2$Se$_3$ surface. Red circles are guide to the eye. (d) SEM image of top surface of S3.
of Se to group-II of $\sim 10 : 1$. The ternary $\text{Zn}_{x'}\text{Cd}_{1-x'}\text{Se}$ and quaternary $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ were grown with the compositions $(x', x$ and $y)$ that yield a near in-plane lattice match to $\text{Bi}_2\text{Se}_3$. The growth was initiated with a low temperature ZnCdSe buffer layer grown at 170°C for 30 seconds, then raised to the optimal II-VI growth temperature of 270°C. The growth rates of ZnSe, $\text{Zn}_{x'}\text{Cd}_{1-x'}\text{Se}$ and $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ were $\sim 4$ nm/min, $\sim 7$ nm/min and $\sim 15$ nm/min respectively. For the ZnSe (sample S1), the thickness of the II-VI layer was 80 nm, while for the $\text{Zn}_{x'}\text{Cd}_{1-x'}\text{Se}$ (S2) and the $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ (S3), the thickness was 150 nm. A fourth sample (S0) was also grown in which a thick layer (20 nm) of $\text{Bi}_2\text{Se}_3$ was grown prior to ZnSe deposition.

4.1.2 Structure characterization

The HR-XRD plot shown in Figure 4.1(a) is a $(2\theta - \omega)$ scan of the $\text{Bi}_2\text{Se}_3$ layer underneath the $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ layer (S3). It exhibits thickness fringes around the $\text{Bi}_2\text{Se}_3$ [006] peak, indicating the high crystalline and interfacial quality of the $\text{Bi}_2\text{Se}_3$ film. From the period of the thickness fringes a $\text{Bi}_2\text{Se}_3$ layer thickness of 9.3 nm was measured, in reasonable agreement with the desired thickness. Similar XRD results were obtained for the $\text{Bi}_2\text{Se}_3$ layers in the other structures reported in this paper. In situ RHEED observations were also used to confirm that the $\text{Bi}_2\text{Se}_3$ layers are of high quality. Streaky RHEED patterns, with six-fold symmetry were constantly observed along [1120] direction of the $\text{Bi}_2\text{Se}_3$ as-grown surface during growth, as seen in Figure 4.2(a). At the same direction, the pattern change to typical pattern for ZnSe [63] right after the II-VI layer deposition initiates, as shown in Figure 4.2 (b). While along [1110] direction of the $\text{Bi}_2\text{Se}_3$ surface, another set of pattern appears as shown in Figure 4.2 (c). Both patterns for II-VI also have six fold symmetry and are 30 degree apart from each other. These patterns were observed on II-VI layers before and identified as a $2\sqrt{3} \times 2\sqrt{3}R30$ degree superstructure [66]. We observe similar patterns for all the II-VI layers described in this paper. Typically, the RHEED pattern initially became somewhat spotty when the II-VI layer growth began, and gradually an elongation of the spots was observed as growth of the semiconductor layer proceeded.

Similar RHEED patterns in ZnSe were previously interpreted [63] as a zinc blend phase.
However, a clear-cut determination of the II-VI phase requires construction of pole figures from the XRD $2\theta - \omega$ scans. The pole figure shown in Figure 4.1(b) demonstrates that our ZnSe, Zn$_{x'}$Cd$_{1-x'}$Se and Zn$_x$Cd$_y$Mg$_{1-x-y}$Se layers have a predominant wurtzite structure. The pole figure of the hexagonal [102] plane was examined using a Bruker Vantec 500 two dimensional detector. A six-fold pattern was observed at 37.97 degree for $2\theta$ and 43.42 degree for $\psi$, in correspondence with wurtzite Zn$_x$Cd$_y$Mg$_{1-x-y}$Se layers [67, 68, 69]. Similar pole figures were obtained for the ZnSe and Zn$_{x'}$Cd$_{1-x'}$Se layers. Thus, wurtzite ZnSe, Zn$_{x'}$Cd$_{1-x'}$Se and Zn$_x$Cd$_y$Mg$_{1-x-y}$Se phases on Bi$_2$Se$_3$ layers were unambiguously identified; they are consistent with our REED patterns in Figure 4.2(b) and (c). The possibility of stabilizing the wurtzite crystal structure in the (Zn,Cd,Mg)Se material system opens new possibilities for the device design. Wurtzite structures possess properties that are different from their zinc-blende counterparts such as fewer glide planes and a polar band structure that may prove advantageous for applications such as piezoelectricity and pyroelectricity. Scanning electron microscopy (SEM) images show a smooth surface morphology (see e.g., Figure 4.2(d)), with no sign of precipitates and with the average surface roughness determined from the atomic force microscope (AFM) scans of $\sim$ 0.8 nm.

Figure 4.3(a) shows $(2\theta - \omega)$ scans of samples S1, S2 and S3. The observed peaks correspond to the (002) planes in the case of ZnSe (S1) and ZnCdSe (S2), as reported in the literature [67, 70]. The reflection from ZnCdMgSe (S3) is in good correspondence to that from S2, since they were designed to have lattice parameters closely matching Bi$_2$Se$_3$. From the scans we determined the $a$-plane lattice constant to be 3.98Å for ZnSe (S1), 4.15Å for ZnCdSe (S2) and 4.13Å for ZnCdMgSe (S3) assuming fully relaxed layers and $c/a$ ratio as previously reported [67, 68]. The data indicates a close lattice match for S2 (0.3%) and S3 ($-0.3\%$) with Bi$_2$Se$_3$ (4.14Å) [71], while S1 has a larger mismatch of $-3.9\%$ to Bi$_2$Se$_3$. Thus, by combining the binary materials at precise compositions to form the ternary and quaternary alloys, near lattice matching to Bi$_2$Se$_3$ can be obtained in the mixed alloy layers.

The full width half maximum (FWHM) of the $(2\theta - \omega)$ scans are 0.130 degree for S1, 0.074 degree for S2 and 0.066 degree for S3. The significantly narrower peaks for the ternary and quaternary layers suggest improved crystalline quality. From the rocking curves in Figure
4 Growth of superlattice

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Figure 4.3: (a) $(2\theta - \omega)$ scans of samples S1, S2 and S3. (b) Rocking curve of samples S1, S2 and S3. The narrowing of XRD peaks indicate that the material quality is progressively improved relative to ZnSe, which has relatively large lattice mismatch to Bi$_2$Se$_3$. Zn$_x$Cd$_{1-x}$Se and Zn$_x$Cd$_y$Mg$_{1-x-y}$Se were designed to match Bi$_2$Se$_3$ lattice.
4.3(b) we also see that the widths of the peaks for S2 and S3 are narrower than for S1; here, the FWHM are 1.72 degree for S1, 1.22 degree for S2 and 1.16 degree for S3. The narrowing of XRD peaks in the rocking curves indicates that the material quality was improved for the two mixed alloy materials S2 and S3 relative to pure ZnSe binary. We attribute this, at least in part, to the closer lattice matching between the $\text{Bi}_2\text{Se}_3$ and the $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ and $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ layers. We note that the rocking curves for all samples are still relatively broad and more detailed studies are underway to optimize the crystalline properties of these layers.

### 4.1.3 Electrical characterization

The CER spectra were measured to establish the electronic properties of the semiconductor layers. CER is a modulated reflectance technique in which an ac modulating voltage ($\sim 1$ kV at a frequency 1000 Hz) is applied to the sample in a condenser-like configuration. The plot of $\Delta R/R$ yields a reflectance spectrum with sharp derivative-like features from which the optical transitions can be obtained [72]. The data for samples S1, S3 and S0 are shown in Figure 4.4. The difference between S0 and S1 is the thickness of the $\text{Bi}_2\text{Se}_3$ layer, which is 20 nm for S0 and 6 nm for S1. In S3 a $\text{ZnCdMgSe}$ replaces the $\text{ZnSe}$ layer, while the thickness of $\text{Bi}_2\text{Se}_3$ layer is kept at 6 nm. The CER spectra for the three samples show sharp excitonic features at room temperature. The transition energy values were obtained from the least-square fits to the first derivative of a Lorentzian lineshape (Figure 4.4). The extracted transition energies on the high energy side of the spectra agree well with the expected room temperature bandgaps of the corresponding II-VI alloy compositions grown: 2.68 eV for S0, 2.69 eV for S1, 2.97 eV for S3 and 2.10 eV for S2. From the lattice constant and bandgap measurements the compositions of S2 and S3 were calculated to be $\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se}$ and $\text{Zn}_{0.23}\text{Cd}_{0.25}\text{Mg}_{0.52}\text{Se}$, respectively. We conclude that the epitaxial II-VI layers display well defined bandgaps as expected for crystalline semiconductors.

At lower energies a new spectral feature emerges in bilayers where the $\text{Bi}_2\text{Se}_3$ layer is very thin (samples S1 and S3). It appears in the $\text{Zn}_{0.23}\text{Cd}_{0.25}\text{Mg}_{0.52}\text{Se}/\text{Bi}_2\text{Se}_3$ structure at 2.24 eV and in $\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se}/\text{Bi}_2\text{Se}_3$ at 1.99 eV (Figure 4.4b and 4.4c), separated by 0.7
Figure 4.4: (a),(b),(c) Experimental CER spectra (black lines) of S1, S2 and S3 respectively. Solid lines (red) are fits to the first derivative of a Lorentzian functional form. The transition energy values obtained from the fits are indicated. The fits to CER spectra were performed using WinPR program version 2.1. Good agreement with the experimental curves was obtained. The lower energy (below 1.3 eV) transitions are not accessible in our experimental setup. The sketches of the corresponding quantum well structures are shown in (d), (e), and (f).
eV from the II-VI spectral peaks. This feature is consistent with upshifted excited states in quantum wells formed in thin TI layers due to quantum confinement (see Figure 4.4d-4e) by large bandgap semiconductor overlayers [73]. Quantum confinement will occur when the width of the well is comparable to the exciton Bohr radius (which in Bi$_2$Se$_3$ is $\sim$ 5 nm [74]) and thus is critically dependent on the TIs thickness, as well as barrier height. The smallest TI thickness was chosen at 6 nm since below this thickness the top and bottom TI surfaces are known to hybridize [75]. For the thicker TI layer (20 nm, sample S0) the energy level shift due to quantum confinement is not observed within our experimentally accessible energy range. This suggests that by changing the II-VI alloy composition a further bandgap engineering of the bulk quantum well states in the TI can be achieved.

Resistivity measurements were carried out to evaluate charge transport properties of the heterostructures. The samples were cut into square shapes and gold electrical contacts were lithographically patterned in a van der Pauw configuration, with e-beam evaporated gold contacting the Bi$_2$Se$_3$ layers through the II-VI layers. As shown in Figure 4.5(a), the magnetoresistance (MR) of the samples S1 and S3 decreases sharply as the magnetic field increases in the low field regime below 1T. This behavior is a hallmark of weak antilocalization (WAL), which is a quantum interference correction to classical MR and a signature of the topological surface states arising from their helical spin texture [76]. The WAL cusps in samples S1 and S3 coincide in the low field region and are well described by Hikami-Larkin-Nagaoka (HLN) [77] theory

$$\Delta \sigma = \sigma(B) - \sigma(0) \approx \frac{e^2}{2\pi^2\hbar} [\ln\left(\frac{B_\phi}{B}\right) - \psi\left(\frac{1}{2} + \frac{B_\phi}{B}\right)],$$

(4.1)

where $\Delta \sigma$ is WAL contribution to magnetoconductance and $B_\phi$ is a dephasing magnetic field. From the fits to Eq. 1 (Figure 4.5(b)) we obtained values of parameter $\alpha = 0.56$ and 0.48 for S1 and S3 respectively, comparable to the best MBE single layer samples with back gate [78] and consistent with a single quantum channel ($\alpha = 1/2$). This gives a strong indication that topological surface states of the Bi$_2$Se$_3$ layer are well preserved after the growth of II-VI semiconductor overlayers.
Figure 4.5: (a) Normalized MR of samples S1 (solid black) and S3 (dashed red) measured at 2 K. The cusp is characteristic of the WAL effect. Inset shows a sketch of the van der Pauw configuration of electrical contacts to the samples. Transport measurements were performed using a Quantum Design Physical Property Measuring System (PPMS). (b) A fit of low-field WAL magnetoconductance $\Delta \sigma$ to Eq. 1 for sample S3.
4.2 Superlattice

Superlattices were grown using two growth chambers connected by ultrahigh vacuum (UHV) transfer modules. The growth conditions we have developed for separate Bi$_2$Se$_3$ layers and Zn$_x$Cd$_{1-x}$Se layers were reported previously [65, 79]. The steps in the growth protocol were as follows. First, a 10 nm Bi$_2$Se$_3$ layer was grown on a sapphire substrate and the sample was transferred in vacuum to the II-VI chamber. Next, the growth of II-VI materials was performed under Se rich environment, with Se: group-II flux ratio of $\sim 10 : 1$. The ternary Zn$_x$Cd$_{1-x}$Se was grown with the composition $x = 0.49$ that yields a near in-plane lattice match to Bi$_2$Se$_3$ [79]. In what follows we will refer to this composition as ZnCdSe. The growth temperature was 270°C, and growth rate was $\sim 7$ nm/min. The sample was then transferred back to the Bi$_2$Se$_3$ growth chamber for the growth of next superlattice period.

Alternating Bi$_2$Se$_3$ and ZnCdSe layers were characterized in real time by reflection high-energy electron diffraction (RHEED). Figure 4.6(a) to (d) show RHEED patterns observed during growth along one of the six-fold symmetry axes of the Bi$_2$Se$_3$ surface. The sample shown here is a seven-period structure. The thicknesses of each ZnCdSe and Bi$_2$Se$_3$ layers are 12 nm and 10 nm, respectively. Figure 4.6(a) and (c) show the patterns of the bottommost and the topmost Bi$_2$Se$_3$ layer of the structure, while Figure 4.7(b) and (d) show the ZnCdSe pattern along the same direction from the bottommost and topmost ZnCdSe layers of the structure, as illustrated in Figure 4.7(e). We conclude that there are no differences in the quality of the RHEED pattern between the bottommost and topmost layers for both Bi$_2$Se$_3$ and ZnCdSe. In particular, the Bi$_2$Se$_3$ pattern appears very sharp and streaky in each repeat, suggesting that the surface recovers well each time Bi$_2$Se$_3$ is deposited. This indicates that the growth of samples with a large number of superlattice periods is feasible. (2$\theta$ $-$ $\omega$) high resolution X-ray diffraction (HR-XRD) scan shown in Figure 4.7(f) displays sharp peaks of Bi$_2$Se$_3$(003), Bi$_2$Se$_3$(006), Bi$_2$Se$_3$(012) as well as the sapphire(006) plane. The inset of Figure 4.7(f) shows a zoom-in view of the region of 2$\theta$ between 23 degree and 30 degree. From the zoom-in view, the large peak at 2$\theta$ $\sim$26.3 degree can be assigned to the zero-order superlattice peak, SL(0) [80].

A high-resolution transmission electron microscopy (HRTEM) image in Figure 4.8(a)
Figure 4.6: RHEED patterns of the sample surface: (a) and (c) are of the bottommost and the topmost Bi$_2$Se$_3$ layers. (b) and (d) of the bottommost and the topmost Zn$_x$Cd$_{1-x}$Se layers, $x = 0.49$. The RHEED images indicate that there are no differences in the quality between the bottommost layer and the topmost layer for both Bi$_2$Se$_3$ and Zn$_x$Cd$_{1-x}$Se. (e) A sketch linking RHEED patterns to their corresponding layers (yellow cylinder on the right represents gold contact across all layers for transport measurements). (f) (2\(\theta\) − \(\omega\)) HR-XRD scan for the sample. Inset: expanded view of the SL(0) peak.
Figure 4.7: (a) HRTEM image of a superlattice sample (grown on a sapphire substrate, S). Zn-terminated (red arrow) and Se-terminated (blue arrow) interfaces indicated in (b) are marked on the image. (b) Atomic structure of the superlattice, with wurtzite $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ abutted by $\text{Bi}_2\text{Se}_3$ (only 1QL is shown for simplicity). The horizontal axis is along the [111] direction. The color scheme here is: Zn (purple), Se (green), Bi (pink). The two interfaces have different structural and electronic properties, see text.
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demonstrates the remarkably sharp interfaces of a ZnCdSe layer sandwiched between two Bi$_2$Se$_3$ layers in a superlattice structure schematically shown in Figure 4.8(b).

HRTEM image of a Bi$_2$Se$_3$ superlattice in Figure 4.8 shows a sharply defined interface between Bi$_2$Se$_3$ underlayers and ZnCdSe overlayers. This is consistent with our previous findings [65, 79] of a relatively easy growth of Bi$_2$Se$_3$ on various crystalline and also on amorphous substrates [81], likely owing to van der Waals epitaxy of Bi$_2$Se$_3$. The HRTEM image agrees with the sharp and streaky RHEED pattern in each repeat. We find that the other interface, where Bi$_2$Se$_3$ overlays ZnCdSe, displays a slight ‘waviness’. This is seen in a magnification HRTEM image of alternating ZnCdSe and Bi$_2$Se$_3$ in Figure 4.8(b). The interface of the first Bi$_2$Se$_3$ layer with Al$_2$O$_3$ substrate is sharp and supports high crystalline quality of Bi$_2$Se$_3$ layer (Figure 4.8(c)), in good correspondence with the sharp streaky pattern observed in RHEED patterns (see Figure 4.6).
Figure 4.8: HRTEM images of a superlattice sample. (a) Bi$_2$Se$_3$ layer on a sapphire substrate with the ZnCdSe overlayer. (b) ZnCdSe and Bi$_2$Se$_3$ alternating layers. (c) A zoomed-in view of the Bi$_2$Se$_3$/Al$_2$O$_3$ interface.
4.3 Summary

In summary, Zn\textsubscript{x}Cd\textsubscript{1−x}Se and Zn\textsubscript{x}Cd\textsubscript{y}Mg\textsubscript{1−x−y}Se layers grown over Bi\textsubscript{2}Se\textsubscript{3} layers display better crystalline quality than ZnSe owing to a closer lattice match to Bi\textsubscript{2}Se\textsubscript{3}. New spectral features detected in CER for very thin Bi\textsubscript{2}Se\textsubscript{3} layers indicate upshifting of the TI's quantum well (2DEG) states due to quantum confinement in bilayers, which can be useful to enhance the topological properties. A clearly observed quantum weak antilocalization (WAL) interference contribution to longitudinal Drude resistivity indicates that the topological properties of interfaces with II-VI layers are retained. We have also demonstrated a successful MBE growth of Bi\textsubscript{2}Se\textsubscript{3}/Zn\textsubscript{x}Cd\textsubscript{1−x}Se superlattices. Our results demonstrate that heterostructures based on topological and band insulators can be successfully grown to advance both device research and fundamental physics.
5.1 Surface dominated transport

5.1.1 Weak antilocalization analysis

To investigate the effects of multilayering on charge transport, resistivity measurements were carried out on samples with Au electrical contacts lithographically patterned in a van der Pauw configuration shown in Figure 5.1(a). The measurements were performed using Quantum Design Physical Property Measuring System (PPMS) in magnetic fields up to 14 Tesla. In the low field regime ($B < 1$ T), the magnetoresistance of the superlattice sample decreases sharply as magnetic field decreases. The observed low-field cusp is a thumbprint
Figure 5.1: a) A sketch of van der Pauw electrical contacts to all layers in the Bi$_2$Se$_3$ (grey)/ZnCdSe (blue) superlattice. Gold contacts at four corners and gold wires connected to them by silver paste are indicated. (b) Sheet magnetoresistance at 2K for the seven-layer superlattice plotted vs. transverse component of magnetic field, $B_\perp = B \cos \theta$. Magnetoresistance (MR) scales with $B_\perp$ in the $\pm$ 1 T range, indicating the 2D character of the observed WAL induced by surface electrons and also a 2D character of the background ‘classical’ MR, which is governed by mean free path ($\sim 10 – 20$ nm, expectedly comparable to the TI layer thickness) rather than much longer ($\sim 150$ nm) dephasing length $l_\phi$. 
5 Charge transfer at interface of the superlattice 5.1 Surface dominated transport

of the weak antilocalization (WAL) quantum interference correction to ‘classical’ resistivity, which in TIs is a signature of topological surface states originating from the topological $\pi$ Berry phase [82]. Figure 5.1(b) shows sheet magnetoresistance for the seven-layer superlattice as a function of magnetic field component perpendicular to the $ab$-plane (normal to the (0001) surface), $B_\perp = B \cos \theta$. Here $\theta$ is the angle between field $B$ and the $c$-axis of the Bi$_2$Se$_3$ layers. The data for all values of $\theta$ collapse on one curve – this scaling of the WAL magnetoresistance cusp with $B_\perp$ demonstrates its 2D character [83, 84]. From the fit to Hikami-Larkin-Nagaoka (HLN) 2D localization theory [77]

$$\Delta \sigma_{xx} = \sigma_{xx}(B) - \sigma_{xx}(0) \approx \frac{e^2}{2\pi^2 \hbar} \left[ \ln \left( \frac{B_\phi}{B} \right) - \Psi \left( \frac{1}{2} + \frac{B_\phi}{B} \right) \right], \quad (5.1)$$

where $\Psi$ is the digamma function, we obtain the number of quantum 2D channels contributing to WAL. In theory, for a single 2D channel the coefficient $\alpha$ is 1/2. $B_\phi$ in Eq. 1 is the dephasing magnetic field $B_\phi = \frac{h}{4e l_\phi}$ related to the dephasing length $l_\phi$ of interfering time-reversed electron paths. The fit yields $\alpha = 3.62 \pm 0.01$ (Figure 5.22(c)), which almost exactly corresponds to seven 2D conducting channels [85, 86] in our seven-layer superlattice. The result is robust and is reproduced in different superlattices (e.g., see also data on a three-period superlattice). Notably, this is a first superlattice structure in which a single surface quantum channel per layer has been achieved [87]. From the fits to Eq. 1 we extract $B_\phi = 0.00705 \pm 0.00006$ T and calculate the dephasing length $l_\phi = 152.8 \pm 0.6$ nm (Fig. 2(c)). $l_\phi$ decreases with increasing temperature (Fig. 2(d)), following $l_\phi \propto T^{-0.46 \pm 0.03}$ in close correspondence with the $\sim T^{-0.5}$ dependence expected from theory in 2D systems. [88]

A superlattice comprising three TI layers separated by ZnCdSe was synthesized using the same growth parameters as the seven-period superlattice discussed earlier. In the three-period superlattice the weak localization correction to conductivity was also found to scale with the transverse component of applied magnetic field (Figure 5.3(a)). From the fits to HLN 2D localization theory the values of $\alpha$ and $B_\phi = \frac{h}{4e l_\phi}$ were obtained (Figure 5.3(b)). $B_\phi = 0.00626 \pm 0.00009$ T and dephasing length $l_\phi = 162 \pm 1$ nm were extracted. The value of $\alpha = 1.51 \pm 0.02$ in the three-period superlattice confirms that in all our superlattices the number of quantum channels contributing to WAL scales with the number of TI layers. The dephasing length $l_\phi$ vs. temperature shown in Figure 5.3(c) follows a $T^{-0.53 \pm 0.04}$ law, in
Figure 5.2: (a) Fit of the change in low-field conductance to 2D weak localization theory (Eq. 1). The shaded region highlights the low-field WAL range bounded by the dephasing field $B_\phi = 7.05 \text{ mT} \ll 1 \text{ T}$. (b) Dephasing length obtained from Eq. 1 vs. temperature follows a power law (red) consistent with theory in 2D.
Figure 5.3: (a) Sheet magnetoresistance plotted vs. transverse component of magnetic field, $\mu_0 H \cos \theta$, at 2 K. The scaling with $\cos \theta$ indicates that the observed WAL cusp is induced by 2D surface electrons. (b) A fit to HLN 2D localization theory to the change in conductance at low fields (< 0.5 T). (c) Dephasing length $l_\phi$ obtained from the fits to HLN theory as a function of temperature. A fit to $l_\phi(T)$ is shown in red.
agreement with the 2D character of WAL.

5.1.2 Shubnikov-de Haas oscillations

To test the topological nature of the observed 2D magnetotransport we performed transport measurements at high fields applied normal to the superlattice’s plane. Shubnikov de Haas (SdH) quantum oscillations in the longitudinal resistivity $R_{xx}(H)$ ($\Delta R_{xx}$ is the longitudinal resistivity with the smooth background subtracted) are clearly observed in the seven period superlattice sample (Figure 5.4(a)). By assigning Landau level (LL) index $n$ to the iminima in the oscillations [89] we obtain the LL index plot shown in Figure 5.4(b). The intercept $\beta$ with the $n$ axis in the high field limit gives a Berry phase of $2\pi \beta = \pi$, using $S_f \frac{h}{eB} = 2\pi(n - \beta)$, where $S_f$ is the extremal cross-section of the Fermi surface and factor $\beta = 1/2$. This is an indication of Dirac surface dominated transport [90]. The Fermi cross-section obtained from the period of SdH oscillations $S_f = 2.98 \times 10^{17} m^{-2}$ corresponds to Fermi wavevector $k_f = 0.031 \, \text{Å}^{-1}$ and gives 2D carrier density of $7.56 \times 10^{11} cm^{-2}$, which is comparable to the best results on single layers. [91] We note that the carrier mobility in our superlattices is an order of magnitude higher than reported previously in other superlattice structures [87]; we associate this with a ‘one-sided’ interfacial charge transfer from ZnCdSe to Bi$_2$Se$_3$ as discussed in next section.

By indexing the minima in Shubnikov de Haas (SdH) quantum oscillations of the resistivity $\Delta R_{xx}(H)$ (blue) and its derivative $dR_{xx}(H)/d(\mu_0 H)$ (red) at 1.9 K (see Figure 5.5(a)), a topological $\pi$ Berry phase was obtained for the three period sample, as shown in Figure 5.5(b).

Thus far, we have the following evidence from both the seven period and the three period sample showing there is topological surface dominated transport in our superlattice samples: weak antilocalization scales with perpendicular component of magnetic field; coherent length vs. temperature follows a $T^{-0.50}$ law, in agreement with the 2D character of WAL; $\pi$ Berry phase can be extracted from Shubnikov de Haas oscillation. These results confirm surface dominated transport is accessed in our superlattice samples, one of the goals of this thesis.
Figure 5.4: High field SdH oscillations. (a) Traces of $\Delta R_{xx}$ (blue) and derivative $dR_{xx}/d(\mu_0 H)$ (red) vs. $1/B$ at $T = 1.9$ K at a magnetic field $H \parallel c$ up to 14 T (a smooth background has been subtracted). The magenta dashed lines indicate the minima of $\Delta R_{xx}$ and the green dashed lines mark the minima of $dR_{xx}/d(\mu_0 H)$. (b) Inverse magnetic field corresponding to the minima of $\Delta R_{xx}$ (blue) and $dR_{xx}/d(\mu_0 H)$ (red) vs. Landau level (LL) indices.
5 Charge transfer at interface of the superlattice

5.2 Charge transfer

Figure 5.5: SdH oscillations in the three-period superlattice. (a) $\Delta R_{xx}(H)$ (blue) and derivative $dR_{xx}(H)/d(\mu_0 H)$ (red) vs. $1/B$ at $T = 1.9$ K measured up to 14 T . $\Delta R_{xx}(H)$ was obtained by subtracting a smooth background. Dashed lines indicate the minima of $\Delta R_{xx}$. (b) A plot of inverse magnetic field corresponding to the minima of $\Delta R_{xx}$ (blue) and $dR_{xx}/d(\mu_0 H)$ (red) vs. Landau level index $n$. 

$\beta = 0.5 \pm 0.01$
5.2 Charge transfer

A single quantum channel per TI layer could indicate that top and bottom TI surfaces in each layer are coupled either through the conducting bulk [8] or via coherent tunneling between them [86, 92]. Here, based on our density functional theory (DFT) calculations we suggest another mechanism that could be at play. The idea is anchored on the inherent asymmetry of the interfaces of Bi$_2$Se$_3$ with wurtzite-structured [79] ZnCdSe in the superlattices of interest. Geometries of wurtzite ZnCdSe and a superlattice are shown in Figure 4.7(b). Inversion symmetry is absent in wurtzite structure. When ZnCdSe is grown over the TI layer, it is likely that cation Zn or Cd is interfaced with the TI because of anionic nature of Se in the TI. Once a ZnCdSe layer is formed on the TI layer, the stoichiometry and charge neutrality of the ZnCdSe layer dictate Se termination just before another TI layer grows over the first ZnCdSe layer (Figure 4.7(b)).

DFT-calculated band structures for six quintuple-layers (6QLs) thick Bi$_2$Se$_3$ with Zn and Se terminated ZnSe layers and for bare 6QLs of Bi$_2$Se$_3$ are shown in Figure 5.6 and 5.7 (for details of the method and the corresponding atomic structures see next section). The purpose of using Zn$_x$Cd$_{1-x}$Se rather than ZnSe in the experiment was to reduce effects of stress caused by lattice mismatch at the interface. Since Cd also plays a role of cation like Zn, replacement of Zn$_x$Cd$_{1-x}$Se by ZnSe would not influence the charge transfer effect of our DFT calculations. The top and bottom TI surface states, colored as red and blue, respectively, in Figure 5.6(a)-(c), are identified from electron charge density distribution as a function of vertical z coordinates [93]. When the interface is terminated with cation Zn or Cd, as shown in Figure 5.6(a), the Dirac cone at the interface substantially moves downward in energy relative to the bottom-surface Dirac cone [64], and the chemical potential (Fermi level) goes up and is shifted to the bulk conduction band. This is due to relaxation of interface geometry and charge transfer ($\Delta Q=0.08$ e per 1×1 unit cell area) from the ZnSe layer to the topmost QL.

The negative $\Delta Q$ at the Zn-terminated interface (blue-hatched) in Figure 5.7(a) indicates charge transfer from Zn(1) dangling bonds to the topological surface. We remark that we have previously demonstrated that the wide band gap ZnSe or ZnCdSe overlayers can enforce
5.2 Charge transfer

Figure 5.6: DFT-calculated band structures for (a) 6QLs Bi$_2$Se$_3$ topped by a ZnCdSe layer with Zn at the interface, (b) 6QLs on top of a ZnCdSe layer with Se at the interface and (c) bare Bi$_2$Se$_3$ 6QLs. In (a)-(c), the dashed lines indicate the Fermi levels $E_F$, and the top and bottom surface states are shown as red and blue, respectively. The arrows in (a) and (b) indicate bands strongly localized onto the topmost Se atoms in the ZnSe layer. (d) A sketch of the experimental structure, with different charge filling of Dirac cones. The top and middle layers in (d) are used for (a), while the middle and bottom layers in (d) are for (b). (e) Bare Bi$_2$Se$_3$ on sapphire has the same charge filling on both surfaces, as long as the substrate strain and surface adatom absorption are negligible. The blue Dirac cone in (d) and both Dirac cones in (e) have small fillings in the upper Dirac cones, unlike the DFT results, because pristine Bi$_2$Se$_3$ samples are typically n-type due to surface defects which were not taken into account in the DFT calculations.
Figure 5.7: Calculated charge transfer $\Delta Q$ between the TI layer and the (a) Zn-terminated and the (a) Se terminated ZnCdSe layer. Note that the vertical scale of (a) differs from that of (b).
quantum confinement of 2DEG quantum well states in Bi$_2$Se$_3$ [79]. However, for the Se-terminated interface, as shown in Figure 5.6(b), the Dirac cone at the interface does not change much relative the top-surface Dirac cone (only a slightly upward shift). The positive $\Delta Q$ peak in Figure 5.7(b) suggests small charge transfer mostly in the interface region which is between Se(2) and Se(3) marked by the horizontal line. See next section for details of the relaxation of interface geometry and the charge transfer for both the Zn and Se-terminated structures. As a result of this interface asymmetry, we state that the top- and bottom-surface Dirac cones in the superlattice are well separated. This separation between the two Dirac cones and the Fermi level crossing only the Dirac cone at the Se-terminated side, are found in our superlattice calculation of the same thicknesses of the TI and ZnSe layers as the two slab calculations. Our proposed scenario would be consistent with a single 2D conduction channel per TI layer in the superlattice, and could possibly account for the observed $\alpha$ values in other systems [8, 86, 92], although it should be noted that Eq. 1 is only an approximate description of weak localization and quantized bulk channels coupled to TI surfaces may also have to be considered [94].

5.3 DFT calculations

We carried out band structure calculations on a bare Bi$_2$Se$_3$(111) layer comprising six quintuple layers (QLs), and on ZnSe(111) films of 16 atomic layers in contact with the Bi$_2$Se$_3$ layer, by using density-functional theory (DFT) code, VASP [95]. The purpose of using Zn$_x$Cd$_{1-x}$Se rather than ZnSe in the experiment was to reduce effects of stress caused by lattice mismatch at the interface. Since Cd atoms at the interface also likely donate electrons to the TI surface, replacement of Zn$_x$Cd$_{1-x}$Se by ZnSe would not affect the charge transfer effect in our DFT calculations. One QL consists of five atomic layers, Se-Bi-Se-Bi-Se, which is about 1 nm thick. Considering the wurtzite structure of ZnSe (Figure 4.7(b), 5.8(a), and 5.10(a)), when the ZnSe layer grows over the TI layer, each Zn cation at the interface can be bonded to three Se anions in the TI surface. As mentioned earlier, the next interface between the ZnSe layer and another TI layer is now Se terminated due to the stoichiometry.
Figure 5.8: (a) Relaxed atomic structure of the Zn-terminated interface used in the DFT band-structure calculation. This relaxed structure differs from the initial interface geometry shown in Figure 4.7(b). For details see the text. (b) Calculated $xy$ planar averaged charge difference $\Delta \rho(z)$ per unit cell area vs. $z$ and (c) zoom-in of (b) near the interface region for the Zn-terminated interface structure shown in (a). Atoms near the interface region after the geometry relaxation are shown.
Figure 5.9: Band structures of (a) an isolated TI layer and (b) an isolated ZnSe layer taken from the relaxed Zn-terminated structure. The arrows in (a) and (b) indicate bands strongly localized onto the topmost Se atom in the ZnSe overlayer.
and the charge balance of the ZnSe layer. We simulated separately the Zn-terminated and Se-terminated interface structures, as shown in Figure 5.8 and 5.10, and in Figure 5.6, in order to examine their effects on electronic band structure. In the Zn-terminated structure in Figure 5.8, the rightmost Se atom was passivated with an H atom, while in the Se-terminated structure in Figure 5.10, the leftmost Zn atom was passivated with an F atom. The similar kind of passivation was applied in other DFT calculations [96, 97].

We used the projector augmented wave (PAW) pseudopotentials [98] and generalized-gradient approximation (GGA) [99] as an exchange-correlation functional. Spin-orbit coupling (SOC) was included self-consistently with the spin projection along the z axis (normal to the QL plane). For the bare Bi$_2$Se$_3$ layer, experimental lattice constant $a = 4.143\text{Å}$ was used [100], with a kinetic energy cutoff of 400 eV and $11 \times 11 \times 1$ $k$-points sampled. For all of our DFT calculations, $k$ points were sampled based on Monkhorst-Pack scheme including the Gamma point. To avoid artificial interactions with neighboring unit cells, a vacuum layer over 40-60Å was added in the unit cell.

It is known that bulk band gaps of zinc monochalcogenides (ZnX; X=O, S, Se, and Te) are underestimated by DFT within the local density approximation (LDA) or GGA [101, 102, 103]. In order to relieve this difficulty, on-site Coulomb repulsion $U$ of 8 eV was included for $d$ orbitals of Zn [101, 104]. With this $U$ value, the band gap is found to be 1.7 eV with the experimental lattice constant of $a = 3.98\text{Å}$ [105], while the gap becomes 1.0 eV with the Bi$_2$Se$_3$ lattice constant of $a = 4.143\text{Å}$ [103]. The band gap did not change when the value of $U$ was lowered to 4.7 or 6 eV. We checked that a hybrid exchange-correlation functional such as HSE06 [106] can enhance the gap to 2.44 eV with $a = 3.98\text{Å}$. However, since the computational cost of the hybrid functional is too high for the Bi$_2$Se$_3$/ZnSe structure of interest, it is not plausible to use HSE06 for our study. For the 6QL-layer with ZnSe, we used a $1 \times 1$ surface atom per unit cell due to high computational cost. For the Zn-terminated interface structure, the $z$ coordinates of the ZnSe film, the H atom, and the topmost QL at the interface, were relaxed within the in-plane lattice constant of Bi$_2$Se$_3$, until the magnitude of the forces exerted on all atoms became less than 0.1 eV/Å. For the Se-terminated structure, the $z$ coordinates of the ZnSe film, the F atom, and the bottommost QL at the interface,
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5.3 DFT calculations

Figure 5.10: (a) Relaxed atomic structure of the Se-terminated interface used in the band structure calculation. (b) Calculated $\Delta \rho(z)$ per unit cell area vs. $z$ and (c) zoom-in of (b) near the interface region for the Se-terminated structure. Note vertical scales of (b) and (c) differ from those of Figure 5.8(b) and (c). Atoms near the interface region are shown in (c).

were relaxed until the same accuracy was obtained. For both the Zn-terminated and Se-terminated structures, a kinetic energy cutoff of 400 eV was used and $11 \times 11 \times 1$ $k$-points were sampled. A vacuum layer of 60 Å was added in the unit cells of both types of interface.

From the DFT-calculated band structures shown in Figure 5.6 4(a)-(c), 5.9(a), and 5.11(a), top and bottom surface states were identified to be states where more than 40% of the total electron density was localized either at topmost or bottommost QL, following the procedure in [93]. Top Dirac surface states are indicated in red, while bottom Dirac surfaces states are in blue. The bare TI layer has doubly degenerate surface-state bands due to inversion symmetry. The double degeneracy is lifted for the Zn-terminated and Se-terminated structures due to broken inversion symmetry.
Figure 5.11: Band structures of (a) an isolated TI layer and (b) an isolated ZnSe layer taken from the relaxed Se-terminated structure shown in Figure 5.10(a). The arrows in (b) indicate bands highly localized onto Se(2).
To understand electronic structure of the Zn-terminated structure (Figure 5.6(a)), we calculated band structures of a Bi$_2$Se$_3$ layer and a ZnSe layer whose geometries were taken from the relaxed Bi$_2$Se$_3$/ZnSe structure. As shown in Figure 5.8(a) and (c), after the geometry relaxation, the distance $d$ between the topmost Se and Bi layers of the TI layer, Se(1) and Bi(1), is increased by 0.89 Å, due to strong bonding between Se(1) and the bottommost Zn atom, Zn(1). Thus, Se(1) seems to belong to the ZnSe rather than to the TI side, after the geometry relaxation. This strong bonding creates bands highly localized onto Se(1) below the Fermi level, as indicated by arrows in Figure 5.9(a) and (b). In addition, it induces a small increase of the Fermi level compared to that of the bare layer and downward shifts of the bottom-surface and top-surface Dirac cones from the Fermi level by 0.19 and 0.26 eV, respectively. The bands marked as arrows in Figure 5.9(a) and (b) are highly localized onto the topmost Se atom in the ZnSe side. To find a charge transfer amount between the TI and the ZnSe layers, we computed a $xy$ plane-averaged charge difference between the Zn-terminated structure and a sum of the isolated TI and ZnSe layers, such as $\Delta \rho(z) = \int_x \int_y \rho_1(x, y, z) dxdy - (\int_x \int_y \rho_2(x, y, z) dxdy + \int_x \int_y \rho_3(x, y, z) dxdy)$, where $\rho_1$, $\rho_2$, and $\rho_3$ are charge densities of the Bi$_2$Se$_3$/ZnSe, the isolated Bi$_2$Se$_3$ layer, and the isolated ZnSe layer with the H passivation, respectively. Here the same unit cell sizes and same DFT parameters were used to obtain the charge densities. The curves in Figure 5.8(b) and (c) show $\Delta \rho$ as a function of $z$ per unit cell area. When $\Delta \rho(z)$ is integrated from $z = 0$ to the middle of Bi(1) and Se(1), we find that $\Delta Q = 0.08$ e per unit cell area (14.86 Å$^2$) is transferred from the ZnSe (and interfacial Se(1)) to the TI and that the charge transfer was mainly spread out to the topmost QL, as indicated in Figure 5.7(a). This is consistent with the feature observed from Figure 5.9(a) and (b) that the Fermi level of the isolated ZnSe layer is higher than that of the isolated Bi$_2$Se$_3$ layer. Now with the charge transfer, the Fermi level of the Zn-terminated structure (Figure 5.6(a)) moves upward and the top-surface Dirac cone is well separated from the bottom-surface Dirac cone.

For the Se-terminated structure (Figure 5.10(a)), we carried out the same procedure as above. The band structure of an isolated TI layer (Figure 5.11(d)) taken from the relaxed Se-terminated structure is almost same as that of the bare layer, Figure 5.6(c), because of
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5.4 Evidence from transport measurements

...a negligible effect of the ZnSe layer on the relaxation of interface geometry. The bands indicated as arrows in the band structure of an isolated ZnSe layer (Figure 5.11(b)) are strongly localized onto the topmost Se atom in the ZnSe side, Se(2), indicated in Figure 5.10(c). The Fermi level of the isolated ZnSe layer is close to that of the isolated TI layer (only 0.2 eV difference). The $xy$-plane averaged charge difference $\Delta \rho(z)$ vs $z$ is shown in Figure 5.10(b) and (c). The maximum charge difference occurs at the midpoint of the interface region (between Se(2) and Se(3)), although the overall magnitude is much smaller than that of the Zn-terminated structure. There is very little charge transfer to either the TI or the ZnSe layer, as presented in Figure 5.7(b). This explains why the top and bottom-surface Dirac cones are close to each other in the band structure shown in Figure 5.6(b) in the previous section.

5.4 Evidence from transport measurements

The charge transfer is confirmed by our transport measurements on related structures. Two sets of samples were fabricated. The first set were two ZnSe/Bi$_2$Se$_3$ (10 nm)/sapphire layers, one of which was grown with Zn enriched interface (sample S1), while the other (sample S2) was grown under the standard protocol [79]. S1-S2 and S3-S4 are schematically drawn in Figure 5.12(a). Mobility and carrier concentrations obtained from Hall measurements are listed in the table in Figure 5.12(b). In sample S1 bulk carrier concentration was found to be higher by $\sim 55\%$ and carrier mobility lower by $\sim 29\%$ than in sample S2. The second sample set comprised a thicker (250 nm) Bi$_2$Se$_3$ sample (S3) capped with ZnCdSe layer and a bare 250 nm Bi$_2$Se$_3$ layer (S4). Again, consistent with charge transfer from Zn termination apparent in the DFT calculations, we found that in S3 relative to S4 carrier concentration was increased by $\sim 57\%$ and carrier mobility was reduced by $\sim 20\%$.

All in all, carrier density of the sample with the Zn-enriched interface is higher than that of the standard Zn-terminated interface, and similarly, carrier density of the sample with the Zn-terminated interface is also higher than that of the bare TI layer, all consistent with the charge transfer from the Zn-terminated interface of the II-VI layer with Bi$_2$Se$_3$. The
Figure 5.12: (a) Sketches of capped and bare Bi$_2$Se$_3$ layers corresponding to samples S1 through S4. (b) A table with carrier concentration and mobility values for samples S1 through S4 obtained from Hall measurements. (c) Sheet carrier density $n_s$ and (d) carrier mobility vs. thickness for single capped and uncapped TI layers and 3-period (3ps) and 7-period (7ps) superlattices (black crosses). In (c) the total carried density is plotted. Sample S5 is an uncapped 29 nm Bi$_2$Se$_3$ layer grown on sapphire. Data from Ref. [8] (red lines) are shown for comparison. Note that both superlattices (3ps, 7ps) have higher carrier mobility than the Bi$_2$Se$_3$ layers of similar thickness (S1, S4 and S5).
Zn-enriched interface was formed by irradiating the TI surface with Zn for 30 s prior to the ZnCdSe growth.

As discussed earlier, Eq. 1 is an approximate two-parameter description of weak antilocalization expected from TI surfaces, and the parameter $\alpha$ is only an appropriate metric for the number of 2D topological surface channels when e.g. weak localization or antilocalization contributions from the quantized bulk 2DEG channels can be ignored [94]. In the samples where bulk contributions are significant (samples S3 and S4) we find $\alpha$ to be very sensitive to the field range in the fits, but very robust in the thin TI layers (samples S1, S2 and the superlattices), as has also been seen in the previous works [8, 107] on MBE films.

### 5.5 Evidence from gating experiments

To further test the effect of Zn at the interfaces we have fabricated backgated structures using 200 micrometer thick SrTiO$_3$(111) as a gate dielectric. Top-surface longitudinal resistivity $R_{xx}$ vs. gate voltage $V_g$ measured at 1.9 K is shown in Figure 5.13(b). Due to the large dielectric constant of SrTiO$_3$ at low temperatures, $R_{xx}$ strongly depends on $V_g$ [108, 109]. The structure of two samples are illustrated in Figure 5.13(a). Figure 5.13(b) demonstrates that a bare Bi$_2$Se$_3$ 10 nm layer (sample S7) is clearly tuned by $V_g$ across the Dirac point which corresponds to the maximum $R_{xx}$ on the negative voltage side. This is similar to the experimental data reported previously [108, 109]. However, after an addition of Zn to the top surface (sample S6), ambipolar transport can not be achieved since the Dirac point is not reached between $-100$ and $100$ V in our experiments, i.e., the Dirac point is located far away from the Fermi level.

### 5.6 Summary

In conclusion, crystalline II-VI band semiconductor layers with a degradation-resistant wurtzite structure [79] were found to stabilize interfacial topological regions of Bi$_2$Se$_3$ layers. From Shubnikov-de Haas quantum oscillations we found that TI layers in a superlattice support a topological Dirac $\pi$-Berry phase.
Figure 5.13: (a) Sketches of samples S6 through S7. (b) Measured top-surface longitudinal resistivity $R_{xx}$ vs gate voltage $V_g$ for a Zn irradiated Bi$_2$Se$_3$ (sample S6, red dashed curve) layer and for a bare Bi$_2$Se$_3$ (sample S7, black solid curve) layer gated through SrTiO$_3$(111) at 1.9 K. The inset illustrates Van der Pauw electrical top contacts.
In these TI/II-VI heterostructures we presented a first demonstration of a single two-dimensional quantum conduction channel per TI layer. Our DFT calculations and transport measurements provide strong evidence for asymmetric interfaces of II-VI layers with TI layers caused by charge transfer from the Zn-terminated top II-VI layers; this asymmetry is considered to be responsible for only one surface per layer contributing to 2D surface transport. One implication of our findings is that a growth process that could include Se irradiated interfaces may prevent charge transfer, thereby improving topological transport parameters. Thus, by using suitable non-topological electronically active spacer layers topological transport can be manipulated and complex nanodevices with vertical registry can be envisioned.
Summary and outlook

The work done in this thesis is focused on enhancing topological surface states contribution to transport properties and to understanding and controlling charge transfer to topological surface/interfaces in the superlattice structures grown by molecular beam epitaxy. We have successfully grown a Bi$_2$Se$_3$/ZnCdSe many-period vertical nanostructures, and achieved surface states dominated transport evidenced by transport measurements. We demonstrated that charge transfer at topological surface can be controlled by choosing suitable abutting and stabilized by the interfacial asymmetry.

Our studies show a path for the future work on topological insulator/conventional semiconductor heterostructures, that may take are several interesting directions. As shown for
ZnCdSe, Zn terminated surface can inject electrons into Bi$_2$Se$_3$, hence cause an upwards band bending. It would be interesting to dope the ZnCdSe layer (or choose other layers) to pull electrons out, so that it can cause a downwards band bending. This would significantly lower the bulk carrier density hence make the surface states more easy to access, and mobility of carriers would also be significantly increased due to disappearance of low mobility bulk carriers. These two can be easily evidenced from Hall measurement. The increased mobility and surface carrier to bulk carrier ratio would make the heterostructure a better candidate for applications like spintronics and quantum computation, and also a host to exotic physics phenomenons like QAHE.

Besides tuning charge transfer, the quantum well structure we mentioned in Chapter 4 also should be explored in the future. A systematic study should be performed, where different thickness of Bi$_2$Se$_3$ (form 3QL to 10QL) should be grown, and how the excited states evolve with well thickness is studied. Different barrier layer material with different barrier height should also be explored.

Superlattice of Bi$_2$Se$_3$ and II-VI semiconductors have various of other applications. We can tune surface plasmon polaritons dispersion by varying the number of units cells in superlattice of Bi$_2$Se$_3$ and dielectric (ZnSe, ZnCdSe or other) [110]. One can also tune topological hetero-nanostructures for thermoelectric applications. By controlling charge transfer at topological interface and tuning of Fermi level, we can move a huge step forward in applications of topological materials.
Bibliography


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