2013

Topological insulator growth and characterization

Nicholas Ross Meyer

Iowa State University

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Topological insulator growth and characterizations

by

Nicholas Ross Meyer

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Electrical Engineering

Program of Study Committee:
Faxian Xiu, Major Professor
David Jiles
Sumit Chaudhary

Iowa State University
Ames, Iowa
2013
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<th>Abbreviation</th>
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<tr>
<td>AB</td>
<td>Aharonov-Bohm</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>AQH</td>
<td>Anomalous quantum Hall</td>
</tr>
<tr>
<td>ARPES</td>
<td>Angle-resolved photoemission spectroscopy</td>
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<tr>
<td>BST</td>
<td>Bi$_2$Se$_2$Te</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive (x-ray) spectroscopy</td>
</tr>
<tr>
<td>MC</td>
<td>Magnetoconductance or magnetoconductivity</td>
</tr>
<tr>
<td>MR</td>
<td>Magnetoresistance</td>
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<tr>
<td>PPMS</td>
<td>Physical properties measurement system</td>
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<tr>
<td>QH</td>
<td>Quantum Hall</td>
</tr>
<tr>
<td>QL</td>
<td>Quintuple-layer</td>
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<tr>
<td>SdH</td>
<td>Shubnikov-de Haas</td>
</tr>
<tr>
<td>SOC</td>
<td>Spin-orbit coupling</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
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<tr>
<td>TI</td>
<td>Topological insulator</td>
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<td>TRS</td>
<td>Time-reversal symmetry</td>
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<td>WAL</td>
<td>Weak anti-localization</td>
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<td>WL</td>
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<td>XRD</td>
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ABSTRACT

Topological insulators are a new class of materials that have recently received a lot of attention due to many novel properties that they have been predicted to possess. A topological insulator is a material that is electrically insulating in the bulk while possessing highly conductive and spin-polarized massless Dirac surface states that are protected against disorder by time-reversal symmetry, allowing for near dissipationless transport of spin on the surface. Additionally, time-reversal symmetry can be broken in a topological insulator by, for example, using elemental doping to induce a ferromagnetic phase in the material. The broken time-reversal symmetry allows for the formation of an energy gap on the surface and is important for many interesting properties in these materials. Currently, much work is being done to improve the ability to study the surface states in these materials by, for instance, improving material quality to lower bulk conduction and by using experimental techniques that can distinguish surface transport from bulk transport such as the two-dimensional weak anti-localization effect. In this work, the foundations and properties of topological insulators will be discussed along with several possible applications of these materials for electronics and spintronics devices. Next, the synthesis and material properties of many kinds of topological insulator materials, both nanostructures and thin films, will be presented. Then, experimental techniques used to study the surface states and differentiate them from the bulk states will be explained. Finally, the results from electronic transport experiments in topological insulator nanostructures of Bi$_2$Se$_2$Te and in thin films of Bi$_2$Te$_3$ with broken time-reversal symmetry will be presented and analyzed.
CHAPTER 1. FUNDAMENTALS OF TOPOLOGICAL INSULATORS

1.1 Introduction

Topological insulators are a recently discovered class of materials that are expected to
display many novel properties which arise due to strong spin-orbit coupling (SOC) which leads
to highly conducting surface states while remaining insulating in the bulk. The band structure
of the conducting spin-polarized surface states are characterized by an odd number of linearly
dispersed Dirac cones with that are robust against the opening of a surface energy gap from
perturbations that do not break time-reversal symmetry (TRS) in the system. These properties
suppress backscattering on the surface and allow for near dissipationless spin-polarized currents
upon the surface. However, there are currently many practical challenges limiting the study
and utilization of the properties of the surface states, including a high density of defects in
grown topological insulator (TI) crystals and the small bulk band gaps (less than $\sim 0.35\text{eV}$)
of known TI materials which conspire to obscure the properties of the surface conduction in
experiments by the overwhelmingly dominant conduction from the bulk.

Additionally, TRS can be broken in the system by, for instance, inducing magnetic ordering
in the material via elemental doping, which will lead to the formation of a surface energy gap if
the magnetization is out of plane of the surface. The magnetization will be responsible for the
splitting of energy of spin-up and spin-down carriers on the surface, which represents the loss of
TRS. Although such a system with broken TRS no longer carries low dissipation spin currents on
the surface, the now massive surface states are also important as many interesting phenomena
are proposed to arise from such a situation such as the anomalous quantum Hall state$^{1, 2}$ and
a novel quantized magnetoelectric effect$^{3, 4}$ which allows for an applied electric field to induce
magnetization parallel to the applied electric field or an applied magnetic field to induce an
electric dipole along the magnetic field direction. Additionally, when a TI is interfaced with a superconductor, it is also expected that a quasiparticle composed of a superconducting vortex with a surface carrier of a TI to act as a Majorana fermion, which acts as its own antiparticle, and have been proposed to be useful in the development of fault-tolerant topological quantum computers\textsuperscript{3}, which are expected to solve many problems, such as integer factorization, much faster than an ordinary computer.

This chapter will introduce the concept of topological insulators and elaborate on their properties and applications. Subsequent chapters will discuss the growth and fabrication of TI materials, procedures for their characterizations, and will look into the study of TI nanoflakes of Bi\textsubscript{2}Se\textsubscript{2}Te and thin films of Cr-doped Bi\textsubscript{2}Te\textsubscript{3}.

1.2 Description of Topological Insulators

The defining characteristic of a topological insulator that distinguishes it from an ordinary band insulator is that the band structure of a TI cannot be continuously transformed into that of any ordinary band insulator without closing the bulk band gap due to strong SOC which inverts the bulk valence and conduction bands, allowing for the classification of insulators into classes based upon which band structures can be obtained from another through continuous transformations\textsuperscript{5}. This is analogous to the exercise in the mathematical subject of topology where surfaces or objects in Euclidean space can be classified according to a topological invariant known as the genus, which represents the number of holes in an object in Euclidean space. Any two objects with the same number of holes can be continuously transformed into one another while objects of different genus cannot be as changing the number of holes would constitute a discontinuous transformation or morphing. The gapless surfaces states which exist within the bulk band gap that are characteristic of TIs are then a result of the closing of the bulk band gap at the interface of a TI with an ordinary insulator or air/vacuum due to the reconciliation between the topologically distinct band structures that meet at the interface and are not, strictly speaking, a property of the TI itself.

The surface states are characterized by Dirac cone dispersion (figure 1.1), meaning that the bands exhibit no curvature and therefore the surface carriers have zero effective mass. The
Figure 1.1 Dirac-cone dispersion on the surface of a TI. Surface states are spin-polarized leading to the spin and wavevector directions to be locked at right angles.

Fermi surfaces of the surface states (which represent the highest energy occupied surface states in momentum or k-space at a temperature of 0 K) as the Fermi energy is lowered are circles that uniformly decrease in magnitude before converging to a single Dirac point and then re-emerge as expanding circles\(^6, 7\). The strong SOC also ensures that the surface states are spin-polarized due to the interaction of the charges motion and the magnetic field it generates to the spin so that the spin state of a surface carrier can be determined from the direction of the wavevector \(\vec{k}\) alone and that there is only one state for each point on the surface bands instead of the two seen from bulk bands (figure 1.1). Due to the topological origin of the surface states, the gapless surface dispersion is robust and can keep its form (without the opening of a surface band gap) even in the presence of perturbations such as defects and impurities that do not break TRS. The topological robustness and the SOC act together to suppress backscattering of surface carriers, allowing for highly conductive surface channels. The topological robustness allows for the surface dispersion to not be altered by the presence of perturbations that do not break TRS and the SOC means that the perturbation cannot cause the backscattering of surface carriers as the perturbation would need to alter the spin orientation too and not just the direction of the wavevector\(^6, 3\).

The topological surface states are also sometimes characterized as being robust against
backscattering due to having $\pi$ Berry’s phase, an additional phase component of the surface carrier wavefunction due to intrinsic curvature in the parameter space describing the possible states of the system\textsuperscript{8,9}, which can arise when the parameters of the Hamiltonian are cyclic. The geometric Berry’s phase is related to the concept of parallel transport and can be understood in terms of how to compare geometric properties, such as angles between vectors, that are at different points on an intrinsically curved space\textsuperscript{8}. The origin of the Berry’s phase can be understood by considering a simple Hamiltonian for the surface states

$$H_0 = v_F(k_x \sigma_y - k_y \sigma_x)$$ \hspace{1cm} (1.1)

where $v_F$ is the Fermi velocity, $\vec{k} = (k_x, k_y)$ is the wavevector and $\sigma_x$ and $\sigma_y$ are Pauli matrices\textsuperscript{10}. In the above equation, units are chosen so that the speed of light $c = 1$ so that energy has units that are the inverse of length. The energy eigenvalues of the operator $H_0$ are $E = \pm v_F k$, which is the correct linear form for Dirac-cone dispersion. Figure 1.2a shows a schematic of the surface states band structure from the above Hamiltonian where one direction in momentum space has been suppressed, or equivalently, where we look at the conducting one-dimensional edge states from a two-dimensional TI. Due to intrinsic curvature in the parameter space for the surface, when a surface carrier is adiabatically transported through a closed loop in parameter space enclosing the Dirac point, it is subject to the extra geometric Berry’s phase due to the curvature of the space\textsuperscript{8}. The important features for the nonzero Berry’s phase is the spin-polarized bands with the single crossing at the Dirac point\textsuperscript{11}. Perturbations that destroy the $\pi$ Berry’s phase can be related to breaking of TRS as a system with Berry’s phase that is neither 0 nor $\pi$ cannot have TRS.

Certain perturbations, such as the application of a magnetic field out of plane of the surface or elemental doping that leads to magnetic ordering out of plane, break TRS in the system by opening a surface energy gap at the Dirac point that now separates the energy states of spin-up carriers from spin-down upon the surface\textsuperscript{12}. The loss of TRS is represented by the energy splitting between the spin-up and spin-down states. In the case of magnetic ordering out of plane of the surface in a TI the surface Hamiltonian can be written as
$H = H_0 + \frac{1}{2} J M \sigma_z$ \hspace{1cm} (1.2)

where $J$ is the dimensionless exchange coefficient, $M$ is the magnetization, $\sigma_z$ is a Pauli matrix, and $H_0$ is the unperturbed Hamiltonian described before. As before, units where $c = 1$ are chosen, giving energy units that are inverse of length. The schematic of the surface bands in this case is shown in figure 1.2b. In this case the energy eigenvalues are given by $E_k = \pm \sqrt{(v_F k)^2 + (\frac{1}{2} J M)^2}$, which describes bands separated by an energy gap of $J M^{10}$. This can be compared directly with the well-known expression for the dispersion of a free relativistic particle, $E_p = \pm \sqrt{(c p)^2 + (m c^2)^2}$ where $c$ is the speed of light, $m$ is the particle mass and $p$ is the momentum. It’s seen that the dispersion characteristics of surface carriers in TIs are much the same as for free relativistic particles, with the magnetization and exchange coupling accounting for the energy gap instead of the particle mass. Due to the introduction of the surface energy gap and loss of the $\pi$ Berry’s phase, surface backscattering would no longer be suppressed and surface carriers would exhibit a non-zero effective mass. It is in this situation, with a surface energy gap, that topological insulators find many of their interesting properties related to the anomalous quantum Hall effect and its quantized conductivity.
1.3 Properties of Topological Insulators with an Induced Surface Energy Gap

Inducing a surface energy gap in a TI capable of magnetic ordering involves keeping a component of the magnetization normal to the surface. In fact, theory and experiment suggest that the surface gap should increase proportionally with the magnitude of the component of the magnetization normal to the surface due to the energy splitting between carriers with spin components parallel and anti-parallel to the magnetization direction, and that the energy gap should close if the magnetization should fall to zero or be completely in plane with the surface opening the possibility of using the magnetization direction to modulate the behavior of the surface between conducting and insulating. There are many possible applications of TIs with an induced surface energy gap, and the energy gap can be created with magnetic ordering, applying an external magnetic field, interfacing the TI with an insulating ferromagnet, or any other mechanism that breaks TRS. Additionally, the surface energy gap can be opened by the superconducting proximity effect and this is important for the discovery of Majorana fermions 13.

1.3.0.1 Anomalous Quantum Hall State

One of the many interesting properties expected to appear in TIs under certain conditions is an analogue of the quantum Hall (QH) effect that can exist without the application of an external magnetic field due to magnetism induced within the material. This effect is known as the anomalous quantum Hall (AQH) effect and just like the QH effect, it allows for quantized conductance on the edge of the sample if there is magnetic ordering in the material1. Specifically, to observe the AQH state in TI materials it is important that the induced surface band gap is within the bulk band gap and that the Fermi level is positioned within both band gaps to put the whole sample in an insulating state. These conditions should be obtainable for certain $x$ in the compound $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ doped with Cr, and in fact there is a report of the first experimental verification of the AQH state in just such a system14.

The conductance of the surface in the AQH state in three-dimensions is quantized in mul-
tiples of \( \sigma_{Hall} = (2n + 1)e^2/2h \) where \( n \) is an integer indicating the number of surface Dirac cones, which is one for typical TI materials such as Bi\(_2\)Se\(_3\). The quantized AQH effect is thought to be related to an interesting coupling between the electric and magnetic fields in TI samples.

1.3.0.2 Magnetolectric Effect

A quantized effect related to the AQH state is known as the magnetolectric effect and is characterized by an electric dipole moment arising within a magnetically doped TI along the direction of an applied magnetic field or, alternatively, the induction of a magnetic dipole moment along the axis of an applied electric field in the surface gapped TI material. This subject often gets referred to as axion electrodynamics as the term added in the action has the same form as a term which describes the interaction of a hypothetical axion field with the electromagnetic field in elementary particle physics\(^3\). In both cases the normal electromagnetic Lagrangian (density) \( \mathcal{L} \) obtains an extra additive term,

\[
\Delta \mathcal{L} = \theta \frac{e^2}{2\pi h} \vec{E} \cdot \vec{B}
\]  

(1.3)

where \( \theta = 0(\mod 2\pi) \) in ordinary insulators, \( \theta = \pi(\mod 2\pi) \) in a TI, \( \vec{E} \) and \( \vec{B} \) are the electric field and magnetic flux density, respectively. It should be noted that \( \theta \) itself has no direct effect on the electrodynamics as only the total derivative of \( \theta \) is present in the equations of motion. At the interface of a magnetically gapped TI where the value of \( \theta \) changes by \( \Delta \theta \), however, the Hall surface conductivity is given by \( \sigma = \Delta \theta (e^2/2\pi h)^3 \). At the interface between a trivial insulator and a TI \( \Delta \theta = \pi \) and the value of the conductance agrees with the value associated with the AQH state discussed previously.

The additional term in the Lagrangian leads to the relations (in Gaussian units)

\[
\vec{D} = \vec{E} + 4\pi \vec{P} - 2\alpha \vec{P}_3 \vec{B}
\]  

(1.4)

\[
\vec{H} = \vec{B} - 4\pi \vec{M} - 2\alpha \vec{P}_3 \vec{E}
\]  

(1.5)
where $\mathbf{B}$ is the electric flux density, $\mathbf{H}$ is the magnetic field, and $\mathbf{P}$ and $\mathbf{M}$ are the polarizability and magnetization, respectively. Here, $P_3 = 0$ for ordinary insulators and $P_3 = \mu_1 / 2$ in TIs\(^4\).

As stated previously, this is related to the AQH effect. If a cylindrical TI with a magnetically gapped surface has an electric field $\mathbf{E}$ pointing along the axis of the cylinder, then the azimuthal surface Hall current $(e^2/2\hbar)|\mathbf{E}|$ gives rise to an overall magnetization $\mathbf{M} = \alpha \mathbf{E}$ where $\alpha = e^2/2\hbar^3$.

### 1.3.0.3 Image Magnetic Monopole

An interesting aspect of the magnetoelectric effect in TIs is that an electric charge near the TI surface can generate not only an image electric charge, but an image magnetic monopole as well\(^4\) that is caused by surface currents induced on the TI surface by the electric charge. The surface currents in this case locally produce the magnetic field that looks like the field of a magnetic monopole. However, there is additionally a line of magnetic charge density induced in the TI that allows for the magnetic flux lines to close, preserving the relation $\nabla \cdot \mathbf{B} = 0$. Over distance scales smaller than the distance between the electric charge and the TI surface, the contribution to the local magnetic field is dominated by the image monopole contribution and it is predicted that the image monopole could be detected by using a magnetic force microscope\(^1\). By solving the equations of motion using the electromagnetic Lagrangian with the additional term $\Delta L = \theta (e^2/2\pi \hbar) \mathbf{E} \cdot \mathbf{B}$ it can be shown that the in-plane component of the electric field created by an electric charge gives rise to the Hall current

$$j = P_3 \frac{e^2}{h} \frac{q}{1 + \alpha^2 P_3^2 (r^2 + d^2)^3/2} \frac{r}{(r^2 + d^2)^{3/2}} \quad (1.6)$$

that circulates on the surface around the electric charge where $r$ is the radial distance and $d$ is the distance from the electric charge to the interface\(^4\). This current gives rise to the magnetic field from the image monopole. Additionally, a coupling between the image magnetic monopole together with the electric charge can form a quasi-particle with fractional statistics, obeying statistical rules intermediate between those of fermions and bosons. Such anyon excitations are allowed in two-dimensional systems and allow for a phase change that can vary between 0 and
π when two identical anyons are exchanged, instead of the phase change of π for fermions and 0 for bosons\textsuperscript{13}.

1.4 Conclusion

Topological insulators are materials that are electrically insulating in the bulk while displaying conducting surface states characterized by Dirac-cone dispersion that is topologically protected from forming a surface energy gap from perturbations that do not break TRS. Additionally, the strong SOC leads to spin-polarity of the surface states that can be understood in terms of a π Berry’s phase and is responsible for the suppression of backscattering on the TI surface. By breaking TRS in the system, a surface energy gap can open that strongly alters the characteristics of surface conduction due to an excitation gap and the resumption of backscattering. However, TIs with broken TRS are expected to exhibit remarkable properties such as the AQH effect and the magnetoelectric effect. In actual TI samples, however, the bulk conduction is often dominant over the surface transport due to perturbations in the crystal that increase conductivity and the small band gaps of known TI materials. The next chapter will focus on the growth of materials used for TI research.
CHAPTER 2. GROWTH OF TOPOLOGICAL INSULATORS

There have been many proposed classes of TI materials, but bismuth and antimony based
binary and ternary compounds are the most studied. The growth of TI crystals is focused on
minimizing defects in order to lower the bulk conduction and allow for the transport properties
of the surface to be more easily differentiated from the bulk. Using nanostructures that have
a large surface area to volume ratio also allows for the suppression of bulk transport relative
to the surface, as can using composition tuning in ternary materials to manipulate the band
structure and Fermi level.

2.1 Introduction

Bismuth and antimony based binary and ternary TI compounds compose by far the most
studied group of TI compounds. Materials that have been studied for their topological surface
states include Bi$_2$Se$_3$, Bi$_2$Te$_3$, (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$, Bi$_2$(Se$_x$Te$_{1-x}$)$_3$, Sb$_2$Te$_3$ and (Bi$_x$Sb$_{1-x}$)$_2$Se$_3$.
The previously mentioned binary materials are known to crystallize in a rhombohedral structure
with space group R$ar{3}$m$^{15}$. The structure can be thought of as consisting of five layer stacks
of staggered honeycomb lattices, each collection of five atomic planes known as a quintuple
layer (QL). The species of atoms varies layer-by-layer as X–Y–X—Y–X for a binary TI of the
form Y$_2$X$_3$. For instance, the Bi$_2$Te$_3$ crystal is made up of stacks of QLs that are arranged
as Te-Bi-Te-Bi-Te, while for the ternary compound (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$, Sb atoms occupy lattice
sites upon the Bi planes$^{16}$. The QLs are weakly bounded to one another by the van der Waals
dipole-dipole interaction and in these materials each QL is $\sim$ 1 nm thick.

Many other materials related to those previously mentioned have also been experimentally
addressed including TlBiSe$_2$, TlBiTe$_2$ and PbBi$_2$Te$_4$$^{17}$. In fact, TlBiSe$_2$ has a relatively large
band gap of $\sim 350 \text{meV}$ and a simple surface state structure, but its study has largely been limited, perhaps due to the toxicity of Tl. Other classes of materials, for instance the half-Heusler family of compounds, are also predicted to host topological surface states. These include for instance LuPtSb, YPdBi, LuPd,Bi, YAuPb, LaPtBi, YPtBi, and LuPtBi$^{18}$, but have not been strongly investigated at this point.

This chapter will explore the synthesis of different varieties of TI nanostructures and thin films and will address some of the differences seen in different materials and growth methods.

### 2.2 Synthesis of Topological Insulator Nanostructures

Nanostructure crystals such as nanoplates and nanoribbons of TIs are important for transport experiments because they allow the surface properties to become more apparent by minimizing the volume of the bulk and thereby suppressing the bulk's contribution to the overall transport. TI nanostructures have been developed by many methods that include metal-organic chemical vapor deposition, solvothermal synthesis, a sonochemical technique$^{19}$, galvanic displacement$^{20}$, and cleaving from a bulk crystal$^{21}$. One of the most useful and common experimental technique for making high-quality TI nanostructures involves a vapor-liquid-solid (VLS) method or a vapor-solid (VS) method if no metal catalyst is to be used.

#### 2.2.1 VS and VLS Growth Techniques

The VS and VLS techniques specify two similar methods for synthesizing TI nanostructures. The two methods differ in that for the VLS technique there are metal nanoparticle catalysts on the substrate whereas no metal catalyst is used in the VS technique. Nanoparticle catalysts help in encouraging uniaxial crystal growth and also can be used for elemental doping$^{22}$. The basic features of the VLS method can be arranged into three distinct stages beginning with the metal alloying with the vapor, followed by nucleation of the crystal, and finishing with axial growth of the crystal$^{23}$. The typical experimental setup for using the VS or VLS technique involves a partially evacuated quartz tube that is nonuniformly heated within a horizontal tube furnace where the tube is connected to a vacuum pump on one end while an inert gas is
introduced into the tube from the other end with its flow rate well controlled using a mass flow controller (MFC).

In a typical experiment, raw source materials contained within glass or ceramic crucibles are placed within a relatively warm region of the tube and the substrate crystal where the nanostructures will form is placed downstream towards the pump end of the tube. The tube is usually pumped down to a low pressure and flushed-out with the inert gas before being set to the final pressure and flow rates to be used during growth. Upon warming the source material, vapors are carried downstream by the inert gas and crystallize into nanostructures on the substrate surface. The properties of the nanostructures can be influenced by parameters such as the source temperature, substrate temperature/location, flow rate, and air pressure.

2.2.2 Topological Insulator Nanostructures by VS and VLS

Many research groups have demonstrated the synthesis of nanostructures of Bi and Sb based TI materials using the VS and VLS techniques. The high quality of these crystals synthesized by these techniques have aided in the characterizations of their surface states of TI materials. Bi$_2$Se$_3$ is known to be promising for TI applications due to the simple surface state structure and relatively large bulk band gap ($\sim$0.3 eV) and many types of nanostructures of that type have been grown and characterized.

2.2.2.1 Bi$_2$Se$_3$ Nanostructures

A Au nanoparticle catalyst has been used by Peng et al. in fabricating single-crystal Bi$_2$Se$_3$ nanoribbons by utilizing the VLS method. The silicon [100] substrates were coated with the Au nanoparticles by placing the substrates into a colloid solution of 20-nm-diameter Au after functionalizing with 0.1 percent w/v aqueous poly-L-lysine solution. Bi$_2$Se$_3$ powder was used as a source material and was placed into the warm central region of the tube furnace. Prior to growth the tube is evacuated to 30 mTorr and flushed with Ar. Finally, the base pressure of the Ar-rich atmosphere is raised to 50 Torr and the source material is raised to 500 C allowing growth to occur for 5 hours before cooling. Nanoribbons were successfully grown from 6-10 cm
from the source and they had typical thickness ranging from 25-100 nm and widths from 50 nm up to several microns\textsuperscript{24}. Grown samples were characterized by the Hall effect and the electron density was found to range between $3 \times 10^{13} \text{cm}^{-2}$ and $2 \times 10^{14} \text{cm}^{-2}$. The carrier density of the nanoribbons can be adjusted by adding 10 percent H\textsubscript{2} to the Ar carrier gas\textsuperscript{25}, altering the growth temperature, post-annealing the sample within a Se dominant atmosphere, or by using a Sn/Au alloy as a catalyst which allows for the doping of Sn into the crystal\textsuperscript{24}.

Sb-doped Bi\textsubscript{2}Se\textsubscript{3} nanoribbons have been synthesized by Hong et al. via the VLS growth method using a thermally grown 10 nm thick Au film coated Si substrate\textsuperscript{29}. The main source material of Bi\textsubscript{2}Se\textsubscript{3} powder was placed into the center of the furnace, while the doping source of Sb\textsubscript{2}Se\textsubscript{3} was placed at an upstream lower temperature location. By placing the doping source at different locations upstream its temperature can be modulated and the Sb concentration can be controlled. For high Sb-doping level (6-7 atomic percent), the bulk carrier concentration can be reduced to $\sim 10^{13} \text{cm}^{-3}$, which suggests surface-dominant transport in Sb-doped Bi\textsubscript{2}Se\textsubscript{3} nanoribbons\textsuperscript{29}. The bulk concentration can be further lowered by preventing exposure of the surface to H\textsubscript{2}O and O\textsubscript{2}\textsuperscript{19} with the use of a capping layer that is 15 nm thick ZnO. The gate dependent transport properties indicated that the Fermi level is very close to the Dirac point and the carrier density was further decreased\textsuperscript{29} to $5 \times 10^{12} \text{cm}^{-3}$.

Nanoplates of Bi\textsubscript{2}Se\textsubscript{3} has been synthesized using the catalyst-free VS method by Kong et al. As before, Bi\textsubscript{2}Se\textsubscript{3} powder was used as the source material and was placed in the warm center of the furnace $\sim 12 \text{cm}$ upstream from the oxidized Si wafer substrate. After pumping down the tube to 100 mTorr and flushing it out with Ar, the source material was heated to 450-500 C while the pressure is held steady at 100 Torr for approximately 5 minutes before being allowed to cool down. The lateral growth rate is much faster than in the vertical growth direction due to the bonding anisotropy, allowing for ultrathin ($\sim$3-6 QL) nanoplates\textsuperscript{19}.

To magnetically dope a nanostructure a Ni-Au or Fe-Au catalyst can be used where the Ni and Fe act as catalysts and magnetic impurities. For synthesis, 2 nm of Ni or Fe can be deposited upon Si [100] and then covered in 5 nm of Au to serve as a capping layer that helps prevent oxidation of magnetic impurities\textsuperscript{22}. Energy dispersive x-ray spectroscopy (EDS) measurements show that the catalyst particles at the top end of the nanoribbons contain magnetic impurities,
suggesting that the impurities are present in the nanoribbon. Temperature-dependent resistance measurements were obtained on Fe-doped Bi$_2$Se$_3$ nanoribbon devices and seem to confirm the presence of the magnetic impurities via the Kondo effect $^{22}$.

### 2.2.2.2 Bi$_2$Te$_3$ Nanostructures

The compound Bi$_2$Te$_3$ is very similar to Bi$_2$Se$_3$ as it crystallizes in the same structure and also has QLs of $\sim$1 nm in thickness, although its bulk band gap is also only about half that of Bi$_2$Se$_3$ and the Dirac point resides within the bulk valence band. Nanoplates of Bi$_2$Te$_3$ have also been synthesized using the same catalyst-free VS method described before with a growth temperature of 450-480 °C and the growth pressure set at 20 Torr$^{19}$.

Kong et al. have used e-beam lithography to fabricate a four point probe on the nanoplates from thermally evaporated Cr and Au. Additionally, a patterned Cr/Au top gate was fabricated atop a Al$_2$O$_3$ layer for this nanoplate device. Resistance measurements are performed at 2 K in a physical property measurement system (PPMS). The response from gating indicates the nanoplates to be n-type due to antisite defects and Te vacancies. Hall measurements estimate the areal carrier density under zero gate bias to be $7.2 \times 10^{13} \text{cm}^{-2} \text{ and } 2.1 \times 10^{13} \text{cm}^{-2}$ for a gate voltage of -20 V$^{19}$.

In an attempt to reduce the bulk conductivity, Na-doped Bi$_2$Te$_3$ nanoplates have been synthesized by a solvothermal method$^{28}$ and had typical dimensions of about 3-6 $\mu$m across and 35-50 nm thick. After fabrication of a six-terminal Hall bar with gating, the nanoplates were characterized by transport methods. At 1.9 K the conduction channel shows n-type behavior for gate voltage between 0 and 80 V as the resistance is decreased by increasing gate voltage, while p-type conduction takes place for gate voltage between -80 and -40 V. Around 40 K the channel resistance is nearly constant from -40 to 5 V. As the temperature rises above 40 K, the transition between n-type and p-type occurs at successively lower gate voltage until finally, near 300 K, the channel exhibit n-type conduction in the full voltage range of -80 to 80 V verifying that under certain circumstances gating a device is useful for tuning and minimizing the bulk carrier density$^{28}$. 
2.2.2.3 Sb$_2$Te$_3$ Nanostructures

Just as for other materials, researchers have synthesized nanostructures of Sb$_2$Te$_3$ using the VLS technique with a Au catalyst. Nanoparticles of Au were immobilized on SiO$_2$/Si by a thin layer of polyelectrolyte and elemental powders of Sb and Te were heated up in a tube furnace under Ar gas flow with the Sb powder placed at the center of the hot zone, the Te 13.5 cm upstream of the Sb, and the Au covered substrates downstream from the precursors$^{27}$. The best location for nanostructure growth was found to be 9-11 cm downstream from the Sb. The type of nanostructure produced varied with the growth conditions. Nanoplates could be grown without the gold catalyst at 430 C and 80 sccm air flow and typically had micron sized edge lengths and were several hundred nanometers thick. Nanowires appear with temperature in the vicinity of $\sim$430 C and flow rate of 80 sccm. By raising the flow rate to 140 sccm, thicker nanobelts of typical widths around $\sim$250 nm can be produced$^{27}$.

Transport properties measurement on Sb$_2$Te$_3$ nanowires with different diameters at room temperature didn’t show a strong diameter-dependence, while at low temperature (below 50 K), the resistances of the nanowires with small diameters ($< 45$ nm) increases to several times of the room temperature value. Magnetoresistance measurement on these Sb$_2$Te$_3$ nanowires showed the perpendicular magnetoresistance is in a parabolic dependence of the magnetic fields up to $\pm$ 10 T at all temperature regimes$^{30}$.

2.2.2.4 (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ Nanostructures

Ternary TI compounds are commonly used as a way of both tuning the bulk conductivity and altering band structure. Single-crystal (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ nanoplates on a 300 nm thick SiO$_2$ film on a Si wafer has been grown with a catalyst-free VS growth method using Bi$_2$Te$_3$ and Sb$_2$Te$_3$ powders as precursors. The lowest intrinsic carrier density is found for the composition (Bi$_{0.50}$Sb$_{0.50}$)$_2$Te$_3$$^{31}$. The Dirac-cone dispersion of surface states were verified by using angle-resolved photoemission spectroscopy (ARPES) on the (0001) plane of (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ bulk crystals of varying compositions. Both experimental and theoretical data suggests the existence of the topological surface states across the entire compositional range.
Using back-gated FET devices the resistance and Hall coefficient can be measured under varying gate voltages. As the gate voltage is swept for very thin (∼5 nm) nanoplates, the resistance is found to have a maximum spike about 50 times as large as the nearly constant resistance seen at positive gate voltages. The Hall coefficient changes sign at the point of maximum resistance suggesting an ambipolar field effect where the nanoplate can be tuned between n-type and p-type under the influence of a gate bias.

2.2.2.5 Bi₂(SeₓTe₁₋ₓ)₃ Nanostructures

Bi₂(SeₓTe₁₋ₓ)₃ nanoribbons were grown using a 10 nm gold film as the metal catalyst using the VLS technique with Bi₂Se₃ and Bi₂Te₃ powders as the precursors by Cha et al. The composition is then tuned by changing the relative amount of each source material. After flushing the tube with Ar at 100 mTorr, the furnace is heated to 500 °C and held for ∼2 hours with an Ar flow of 30-150 standard cubic centimeters (sccm). Nanoplates were grown in a similar fashion to the nanoribbons except that the growth is directly on SiO₂, the growth temperature is 480 °C, and it is held there for 10 minutes. For the compound Bi₂(SeₓTe₁₋ₓ)₃, the carrier density in the nanoribbon was seen to decrease with x. Since the carrier density is lower for the nanoribbons than for nanoplates for a given x, nanoribbons were focused on in transport experiments.

A six-terminal Hall bar was constructed using e-beam lithography and thermal evaporation of Cr/Au for metal contacts. From Hall measurements done at 2 K on Bi₂(Se₀.₃₄Te₀.₆₆)₃, the two-dimensional carrier density is found to be \( n = 1.69 \times 10^{14} \text{cm}^{-2} \) and the Hall mobility is \( 28 \text{cm}^2/\text{Vs} \), which is much lower than the mobility in Bi₂Se₃ bulk or nanostructure samples.

2.3 Synthesis of Topological Insulator Thin Films

Nanostructures are useful in TI research by allowing surface conduction to not be overwhelmed by the bulk conduction. TI thin films, in particular those grown by molecular beam epitaxy (MBE), also have certain advantages that make them attractive for research. In this section we will restrict ourselves to TI thin films grown by MBE. Materials grown using this method allow us to achieve very high quality crystals and allows us to precisely control ele-
mental doping. Additionally, MBE allows for very smooth surfaces which could be useful in enhancing the surface carrier mobility and also for creating clean heterostructures for device applications.

### 2.3.1 Molecular Beam Epitaxy

Molecular beam epitaxy (MBE) is a thin film crystal fabrication technique which takes place in ultra-high vacuum and allows for the growth of a crystal on a seed substrate crystal by heating the substrate and also heating elemental source materials, allowing the source vapor pressures to rise and for the vapors to deposit upon the surface of the substrate crystal where they react with other vapors and the substrate to form a thin film crystal on the surface of the substrate. For high quality single-crystal film, the substrate crystal and the thin film to be grown on it should have similar crystal structures with similar lattice constants to allow for the film to grow epitaxially without causing much lattice strain and defects at the interface. The main advantages of MBE are the low number of impurities due to the process being done in a high vacuum environment, and the low number of lattice defects due to the ability to influence the growth rate and ratio of species of source materials present at the substrate interface. Additionally, as crystals can be grown layer by layer, the crystal surfaces can be atomically flat, allowing for smooth interfaces and precisely engineered heterostructures.

In MBE, source materials are kept in ceramic crucibles and are housed in effusion cells which contain a heater cupping the crucible, a thermocouple for measuring the crucible temperature and vacuum feedthroughs to allow external electronics to control the power to the heater and regulate the source material temperature. The temperature can be well controlled to within \( \sim 0.1 \) C, allowing for the control of the relative number of each species of atoms interacting at the substrate surface, which allows us to tune the concentration of doped impurities into the material. The crucible is covered by a pneumatically operated shutter, which can block the source material and limit its diffusion into the growth chamber (figure 2.1). When the shutters opens, the diffusing source materials are known as beams as the atoms often have long mean free paths (\( \sim 40 \) km) due to the high vacuum environment.

The growth chamber contains a heater on which the substrate crystal can be mounted and
manipulated in its orientation relative to the source materials. The heater is usually partially surrounded by liquid nitrogen cooled cryo-shrouds that help lower the growth chamber pressure and act as sinks for the emitted source material. It is common to monitor the quality and growth rate of the crystal during the growth using reflection high-energy electron diffraction (RHEED). With RHEED, a beam of electrons is incident upon the surface of the crystal at a low grazing angle and the interference pattern of the reflected beam is viewed upon a phosphor screen on which the electrons collect. The absence of a pattern will signal that the film is amorphous. The high-quality crystals that grow layer-by-layer will have a RHEED pattern of many streaky lines. If the crystal grows in such a way that the surface is rough, the lines will each discretize into a set of points on the previous line. Growth chambers also typically house a residual gas analyzer which is a mass spectrometer that allows for the relative number of different species of gases in the vacuum chamber to be measured.

MBE growth chambers are regularly capable of achieving ultra-high vacuum, corresponding to at least $\sim 10^{-9}$Torr. To achieve this special consideration is needed to use materials that maintain a low vapor pressure in the range of operating temperatures for the construction of the

Figure 2.1   Schematic of an MBE growth chamber.
MBE system. The flanges connecting the vacuum chamber components are sealed by special conflat flanges that each have a knife-edge which can be pressed into a copper gasket seal by bolting the two flanges together. The soft copper metal can then fill in the gaps between the two flanges and allows for a seal which can maintain vacuum levels of $\sim 10^{-13}\text{Torr}$. Additionally, to achieve ultra-high vacuum MBE vacuum chambers are typically covered in insulating blankets and heated to ”bake-out” the system and allow for atoms and molecules adsorbed to the wall to be released into the chamber due to thermal energy and pumped away by an ion or cryopump capable of maintaining ultra-high vacuum. The high vacuum environment allows for the elemental composition of grown materials to be highly controlled by limiting contamination from impurities within the vacuum chamber atmosphere and by being able to precisely tune the relative vapor pressures of the source materials using temperature controllers to operate the heaters for the source materials.

Despite the advantages of using MBE for TI thin film growth due to high-quality of grown materials and precise doping control, there are challenges in creating thin films of $\text{Bi}_2\text{Se}_3$ and $\text{Bi}_2\text{Te}_3$ with a low enough defect density to allow the Fermi level to exist within the bulk band gap and allow the bulk to be at its most insulating, although this can be alleviated with doping\textsuperscript{33, 34, 35}. Ternary compounds such as $(\text{Bi}_{x}\text{Sb}_{1-x})_2\text{Te}_3$ are useful as they seem to exhibit TI surface states at all compositions and allow for the tuning of the Fermi level and band structure and MBE grown films have been useful in research\textsuperscript{16}. In fact, much work has been done to grow the Bi and Sb based TI compounds mentioned earlier by MBE and in fact they have been successfully grown on many substrates including Si(111)\textsuperscript{35}, Si(111)-7x7\textsuperscript{33}, 6H-SiC(0001), sapphire (0001), SrTiO\textsubscript{3}(111)\textsuperscript{34}, CdS(0001)\textsuperscript{36}, GaAs(111)\textsuperscript{37}, and GaAs(001)\textsuperscript{38}.

In our lab, a Perkin Elmer 430 molecular beam epitaxy system was used to create thin films of TI materials such as $\text{Bi}_2\text{Se}_3$, $\text{Bi}_2\text{Te}_3$, and $\text{Sb}_2\text{Te}_3$ which could be doped by sources such as Cr, Gd, Cd, Mn, and Sb. The MBE was originally used to grow III-V materials and had been disassembled at one point before being reassembled and left idle for several years before being recovered by us. Initial problems with the system included an unworkable mechanical substrate transfer system within the MBE, numerous missing or broken pieces of electronic equipment, contamination from old source material from previous use, broken pumps, and
several leaks within the vacuum chamber. Early samples out of the MBE chamber were of low quality, partially due to the contamination from previous source materials and contaminants that would desorb from the walls of the growth chamber. After repeated use, the walls were coated in the source materials now typically used, and the purity of the films improved allowing for other parameters such as the relative source temperatures and the substrate temperature to be varied to optimize the film quality. Film quality also improved upon discovering several leaks in the system which limited the base pressure from reaching the ultra-high vacuum level of \( \sim 10^{-11}\text{Torr} \) that the system was eventually able to keep. Leaks were discovered using methods such as watching for pressure spikes in the system after introducing mechanical vibrations and spraying acetone along seals as acetone that is able to get into the vacuum chamber can cause a large spike in the pressure reading. Due primarily to the pressure leaks and previous contamination as well as initial instability in the growth parameters and temperature controllers, over one hundred samples had to be grown on various substrates before finally achieving a thin film crystal of Bi\(_2\)Te\(_3\) with an atomically flat surface on mica.
CHAPTER 3. CHARACTERIZATION OF TOPOLOGICAL INSULATORS

One of the prominent challenges in TI research is observing characteristic signs from the surface states that allow their properties to be differentiated from the bulk states. The main material setbacks for experimentally determining the TI surface states are the small band gaps present in these materials and the strong bulk conduction due to perturbations from the ideal crystal structure in grown materials, as was discussed in the last chapter. This chapter will explore some experimental techniques that are useful in determining the properties of the surface states including imaging the band structure from photoemission experiments, observing quantum oscillations via the Aharonov-Bohm and Shubnikov-de Haas effects, and through the weak anti-localization characteristic of the two dimensional surface states.

3.1 Introduction

Due in part to the small band gaps present in all known TI materials (∼ 300 meV or less), confirming and studying the properties of the surface states has been challenging. The first experimental verification of the surface states of topological insulators in the popular Bi, Sb, Se, and Te based binary compounds comes from angle-resolved photoemission spectroscopy experiments\textsuperscript{15} that image the band structure and reveal Dirac cone dispersion between bulk bands, characteristic of TIs. Although magnetic fields applied to TI materials can destroy the Dirac-cone dispersion of the surface states by creating a surface band gap, several experiments using magnetic fields can still be utilized to study the surface states. Subsequent experiments performed on TI nanostructures extract information about the surface states by looking at oscillations in the material resistance upon varying the magnitude of an applied magnetic field.
The oscillations in the resistance can have many origins; among them are oscillations due to the Aharonov-Bohm effect and Shubnikov-de Haas oscillations. Additionally, the weak anti-localization effect in two-dimensions can allow for the existence of the surface states to be inferred from the response of the samples resistance under a small magnetic field. Each of these techniques will be discussed in turn.

### 3.2 Angle-Resolved Photoemission Spectroscopy

Angle-resolved photoemission spectroscopy (ARPES) is an experimental technique for constructing parts of the band structure of a material by probing the density of states and is ultimately based upon the photoelectric effect. A simple model for explaining the photoemission process consists of three parts. An electron in the material is first excited by an incident photon, then travels to the sample surface, and finally escapes the sample. With the aid of an electrostatic analyzer the emission angles relative to the surface and the kinetic energy of the ejected photoelectrons is measured for various incident photon energies and angles. The photon beam often comes from a synchrotron source which allows for a tunable monochromatic source of high intensity.

From the APRES data, the density of states and ultimately reconstruction of parts of the band structure is possible. APRES has been used to confirm the linear Dirac-cone nature of the surface states for many materials and has also been used to study the influence of the induced surface gap due to magnetic ordering.

### 3.3 Aharonov-Bohm Effect

The Aharonov-Bohm (AB) effect, first predicted by Ehrenberg and Siday in 1949, has been of significant interest to physicists as it seems to cause problems in formulating Maxwell’s equations as a gauge theory by not allowing freedom in the choice for the electromagnetic potential used to represent a given electromagnetic field. The most common description of the AB effect involves the phase change of the wavefunction of a charged particle that is moving around a solenoid due to magnetic flux passing along the axis of the solenoid. The phase change
occurs even if the magnetic field is zero everywhere the particles wavefunction is non-negligible and can be understood to occur due to a coupling between the electromagnetic potential with the phase of the wavefunction.

The effect is interesting from a physical prospective because, as noted earlier, the gauge invariance of Maxwell’s equations imply that there should be freedom in choosing the electromagnetic potential because there are infinitely many potentials that equally well describe any one electromagnetic field, while the AB effect shows that the electromagnetic potential has real physical consequences because it couples with the wavefunction to produce phase shifts in the wavefunction. The AB effect in solenoidal geometry is well studied and can be understood by choosing a gauge such that the vector potential \( \vec{A} \) is non-zero, but the magnetic field \( \vec{B} \) is zero so that \( \vec{B} = \nabla \times \vec{A} = \vec{0} \). In this case a charged particle along the outside of the solenoid will acquire a phase shift of \( 43 \)

\[
\phi = \frac{e}{\hbar} \int_{P} \vec{A} \cdot d\vec{x}
\]  

The effect has been used to help study the surface states of topological insulators as the phase shift induced on the surface electrons in a TI by a magnetic field will cause periodic changes in the conductivity of the surface as the magnetic flux passing through the material is varied. In experiments, Bi\(_2\)Se\(_3\) nanoribbons have been used to study the surface states via the AB effect. The relatively simple geometry of the nanoribbon and its similarity of the surface to a solenoid allow for easy analysis of the AB effect in TI materials. In the experiments a magnetic field is applied along the long axis of a Bi\(_2\)Se\(_3\) nanoribbon that has been equipped with a four-point probe device with Ti/Au ohmic contacts. The magnetoresistance can then be measured using a physical property measurement system (PPMS).

The phase change due to the AB effect is given by \( 2\pi \Phi/\Phi_0 \) where \( \Phi \) is the magnetic flux and \( \Phi_0 = h/e \) is the magnetic flux quantum where \( h \) is Planck’s constant. The dominant frequency at which the resistance oscillates is given by \( \Delta B = \Phi_0/A \) where \( A \) is the cross-sectional area of the nanoribbon. There is also a weaker higher order harmonic oscillation where the flux is given by \( h/2e \). Researchers have reported on the AB effect in magnetoresistance oscillations
of a Bi$_2$Se$_3$ nanoribbon by measuring the resistance when the applied magnetic field is in the range of -9 T to +9T. It was found that the dominant oscillation frequency was $\Delta B = 0.62T$, while the measured cross-sectional area of a nanoribbon was found to be $A = 6.6 \times 10^{-15} m^2$. These measurements produce an estimate for $h/e$ to be roughly $4.09 \times 10^{-15} Tm^2$, which differs from the best estimates of $h/e$ by about 1 percent. In the same experiment, the effect of the temperature on the oscillation amplitude was observed and it was found that most of the oscillatory behavior was present up to 20 K$^{24}$.

### 3.4 Shubnikov-de Haas Oscillations

The use of Shubnikov-de Haas (SdH) oscillations for studying surface states in TIs are much like using AB oscillations in many ways. Similar to AB oscillations, periodic changes in the magnetoresistance are measured in order to extract information about the surface states. The origin of the periodic change in magnetoresistance, however, is different in the SdH effect.

![Figure 3.1 Longitudinal resistance of a Bi$_2$Se$_2$Te nanoflake for large magnetic fields. The SdH oscillations are revealed upon removal of the parabolic background.](image)

When exposed to a magnetic field normal to the surface, the Dirac surface states of a TI are quantized into Landau levels (LLs). The energy of the levels is given by $E_n = v_F \sqrt{2n\hbar eB}$, where $v_F$ is the Fermi velocity, $n$ is an integer known as the LL index, $\hbar$ is the reduced Planck’s
constant, $e$ is the electron charge, and $B$ is the magnetic field. The conductance of the sample changes periodically as the magnetic field is increased because the spacing of the quantized levels will change, leading to peaks in conductivity when the Fermi level is at the midpoint of a LL, and reaching a minima when it lies between two LLs\textsuperscript{45}. In our lab, SdH oscillations have been used to study the surface states of Bi$_2$Se$_2$Te nanoflakes, as will be discussed in the next chapter. The extraction of the SdH oscillations from the magnetoresistance measurements is shown in figure 3.1 where the longitudinal resistance of the nanoflake at magnetic fields between $\sim 5T$ and $\sim 9T$ is shown. Upon subtraction of the classical parabolic dependence of the resistance to the magnetic field, the SdH oscillations are revealed.

SdH oscillations in a back-gated Bi$_2$Te$_3$ nanoribbon have also been studied at low temperature under a variety of gate voltages by Xiu et al\textsuperscript{26}. A field-effect transistor device is fabricated on a SiO$_2$ layer of a p++ Si substrate with a Ti/Au electrode as the back-gate. At 1.4 K, the magnetoresistance shows no SdH oscillations under zero gate bias. The hole carriers are partially depleted and the bulk begins to conduct less when a positive gate voltage is applied. As a result, SdH oscillations in the magnetoresistance are seen to grow in amplitude as the gate voltage is swept from +20 V to +80 V. Under a negative bias, holes are induced in the bulk leading to no discernible signal from SdH oscillations of the surface states. The same results are obtained at 4 K except the amplitudes of the SdH oscillations are diminished. After measuring the magnetoresistance, additional parameters can be calculated, including the transport lifetime $\tau$, mean free path $\ell = v_F \tau$, and mobility $\mu = e\tau/m_{cycl} = e\ell/(\hbar k_F)$ by obtaining the best fit of

$$\log\left[ \frac{\Delta R}{R_0} B \sinh \lambda(T) \right] \approx \frac{2\pi^2 E_F}{\tau e B v_F^2}.$$  \hspace{1cm} (3.2)

where $\Delta R$ is the magnetoresistance, $B$ is the magnetic field, $\lambda(T) = 2\pi^2 k_B T m_{cycl}$ with $k_B$ being the Fermi vector, $T$ being the temperature, $m_{cycl}$ the cyclotron mass, and $E_F$ and $v_F$ are the Fermi energy and Fermi velocity, respectively. The factor $\lambda(T)$ can be found from temperature-dependent conductivity measurements as
\[
\frac{\lambda(T)}{\sinh(\lambda(T))} = \frac{\Delta \sigma_{xx}(T)}{\Delta \sigma_{xx}(0)}
\]

where \(\Delta \sigma_{xx}(T)\) is the change in conductivity at temperature \(T\). For Bi\(_2\)Te\(_3\) nanoribbons the estimated values of these parameters are \(\ell = 114\text{nm}\) and \(160\text{nm}, \mu \sim 4560\text{cm}^2/\text{Vs}\) and \(\sim 5790\text{cm}^2/\text{Vs}\), and \(\tau \sim 3.1 \times 10^{-13}\text{s}\) and \(\sim 4.3 \times 10^{-13}\text{s}\) for a gate voltage of +40 V and +80 V, respectively.

### 3.5 Weak Anti-Localization

Weak anti-localization (WAL) can be understood to be related to the fact that on the surface states of TIs are robust against backscattering due to the strong SOC together with the topologically robust Dirac-cone dispersion, leading to a lower resistance than would be expected from similarly dispersed surface states that are not spin-polarized and still allowed for backscattering. By introducing a magnetic field the surface energy gap opens and now separates opposite spin states allowing for surface carriers to backscatter and causing an overall increase in the resistance of the material due to the suppression of WAL\(^{46, 47, 32, 48, 49, 50}\). In fact, since the effective mass is related to the degree of localization of a state and the effective mass of a state depends upon the curvature of the surface bands, it is easy to understand that since the magnetic field will influence the surface band gap, it also forces the surface carriers to become more localized. Additionally, there is the related weak localization effect (WL) that occurs in TIs with strong magnetic disordering and leads to a positive correction to the classical resistivity. Applying a magnetic field will, like with WAL, suppress WL and in this case cause a lowering in the resistance.

A two-dimensional system can be shown to exhibit WAL when TRS is preserved if the change in conductivity of the sample upon breaking the TRS with the application of the magnetic field \(B\) is given by the Hikami-Larkin-Nagaoka (HLN) equation\(^{46}\):

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

where \(\alpha = -1/2\) for WAL and \(\alpha = 1\) for WL and \(\psi\) is the digamma function and \(B_{\phi} = \hbar/4e\ell_{\phi}^2\)
with \( \ell_\phi \) being the coherence length, \( \hbar \) is the reduced Planck’s constant, and \( e \) is the electron charge. WAL can be used to detect the surface states of TIs by looking at the magnetoconductivity from Hall measurements and fitting to the HLN equation. A fitted value for \( \alpha \) near \(-1/2\) suggests one 2D conducting surface without backscattering\(^{51, 52, 53, 54}\).
CHAPTER 4. RESULTS OF A STUDY ON THE SURFACE STATES IN BI$_2$SE$_2$TE NANOFLAKES

4.1 Introduction

Nanostructures provide a good platform for studying TIs as the increased surface area to volume ratio allows for the bulk to contribute less significantly to the overall transport. In this experiment, a high-quality single-crystal ingot of Bi$_2$Se$_2$Te (BST) was created using the Bridgman method for the purpose of studying the structural and transport properties of BST nanoflakes. Using an auger microprobe the elemental composition was measured along the length of the ingot. Mechanical exfoliation was used to cleave thin nanoflakes from the single crystal. The nanoflakes crystal properties were then characterized via transmission electron microscopy (TEM). Electronic characterizations of our BST nanoflake were made using ARPES and a physical properties measurement system (PPMS) for temperature-dependent magneto-resistance (MR) and Hall transport measurements. ARPES measurements show the linear dispersion characteristic of the surface states. Additionally, the observed SdH oscillations and WAL allow us to extract some surface state parameters such as carrier coherence length and transport lifetime.

4.2 Experiment and Measurements

A high-quality single-crystal ingot of Bi$_2$Se$_2$Te was created using the Bridgman technique for the purpose of structural and electronic characterization. From elemental sources the proper ratios of high purity bismuth (99.999%), selenium (99.999%), and tellurium (99.999%) were mixed and sealed in a quartz tube. The sealed mixture was then heated in an induction furnace to melt the mixture and homogenize the composition. Later, the ingot was sealed in a large
diameter quartz tube and loaded into a Bridgman furnace. After heating the materials to 800 C the quartz tube was withdrawn at a rate of 1\text{mm/hr} allowing the composition to crystallize. The crystal composition was studied using a JEOL JAMP-7830F Auger Microprobe and it was found that along the length of the ingot, the relative compositions of Bi, Se, and Te varied less than 3%, suggesting uniformity in the composition throughout.

From the original crystal ingot, thin flakes with characteristic sizes of several micrometers in length and width were mechanically exfoliated and transferred onto a holey carbon copper grid for TEM characterizations using a FEI Tecnai F20 TEM operating at 200\text{kV}. After establishing that the grown crystals were high-quality and of proper composition, experiments could be performed to study the electronic structure and transport properties of the cleaved flakes. Using beam line 12.0.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory, high-resolution ARPES measurements could be made to visualize the electronic band structure of the Bi$_2$Se$_2$Te nanoflakes. To prevent the atmosphere from contaminating the surface and obscuring the properties of the surface, measurements were made in a vacuum better than $5 \times 10^{-11}$ Torr and samples were cleaved in situ prior to performing the experiment. Data was collected using a VG-Scienta SES100 electron analyzer at low temperatures ($< 50K$) using photon energies ranging from 30 to 80 eV.

Finally, transport measurements were performed on nanoflakes that have been fashioned into the standard six-terminal Hall geometry. The device size was 0.5 mm wide and 0.05 mm thick, while the voltage contact distance was 0.6 mm. Room-temperature cured silver paste was used to make ohmic contacts with the sample and simultaneous measurements of the longitudinal resistance $R_{xx}$ and the transverse resistance $R_{xy}$ were made with a Quantum Design physical properties measurement system (PPMS-9T) which has the capability of sweeping the magnetic field between $\pm 9T$ at temperature as low as 1.9K.

4.3 Results

After growth of the bulk BST crystal, TEM characterizations were performed to examine the crystal properties. Figure 4.1a shows a low-magnification TEM image for a BST flake that we mechanically exfoliated from a bulk crystal and shows its size to be several to tens of microns
in width and length. The high-quality rhombohedral phase of the material can be discerned from the sharp selected-area electron diffraction pattern seen in figure 4.1b. High-resolution TEM images allow for the determination of the atomic plane spacing to be 0.22 nm (figure 4.1c) which is consistent with the known d-spacings of the (1120) planes in BST. The powder X-ray diffraction (XRD) pattern shows deviations from an ordered skippenite structure, perhaps suggesting a disordered occupation of Te and Se on the outer two layers of the QL (figure 4.1d). The partially disordered BST structure resulting from random Te substitutions of Se atoms in the outer QLs differs from the central-layer substitution found in Bi$_2$Te$_2$Se (BTS) and conform to the Hume-Rothery solid-solution rules due to the low-energy structure.

Furthermore, the powder XRD refinement experiments confirm such a disordered occupation of Te and Se on the outermost quintuple layers (QLs) and present the non-stoichiometric formula of Bi$_{2}$Se$_{1.88}$Te$_{1.12}$ for the examined crystal. This is in good agreement with previous XRD experiments on a solid solution of Bi$_2$Te$_{3-x}$Se$_x$.

Upon verifying the crystal properties of the BST flakes, high-resolution APRES experiments were performed under varying photon energies to help verify the dispersion of the surface states. Figure 4.2a shows an APRES image of the dispersion around the center of the surface Brillouin zone with a discernible “V” shape linear surface dispersion that is easily resolved above the Dirac point, giving strong evidence for the presence of Dirac fermions. In this sample, the Fermi level is located ∼ 0.3 eV above the Dirac point, which is lower than the reported value of 0.425 eV. One important observation from the APRES spectrum revealed under a series of different photon energies (figure 4.2b) is that the surface dispersion is robust at each excitation energy and the Fermi level intersects only the Dirac cone and the conduction band is not visible in the ARPES spectrum. This is favorable in searching for an ideal TI candidate as it shows that this material is close to being in its insulating state. Additionally, the Dirac cone intersects the Fermi level at a wavevector of magnitude 0.07Å$^{-1}$, which corresponds to a Fermi velocity of $6.4 \times 10^5 m/s$ by momentum distribution curve fitting, which is close to a previously reported value.

With strong evidence of the surface states revealed through the linear dispersion in ARPES experiments, it becomes important to further study the surface state properties via transport
measurements. BST flakes fashioned into a standard six-terminal Hall bar had their transport properties measured using a PPMS. The longitudinal resistance $R_{xx}$ increases roughly two orders of magnitude upon cooling the sample from room temperature towards 1.9 K, indicating non-metallic behavior\textsuperscript{57, 63, 58, 62} (figure 4.3a). The lower inset of figure 4.3a shows the Arrhenius plot of $R_{xx}$, and it shows thermal activation in a temperature range from 300 K down to 120 K. Using the relation $R_{xx} \sim e^{-E_a/k_BT}$, where $E_a$ is the activation energy and $k_B$ is Boltzmann’s constant, the activation energy is found to be around 100 meV. This value is four times larger than the 23 meV of BTS\textsuperscript{57}, but remains on the same order of magnitude to that of Sn-doped BTS\textsuperscript{64}. Fitting to the three-dimensional (3D) variable-range hopping (VRH)\textsuperscript{57, 65}
Figure 4.2  ARPES characterization of BST. (a) ARPES image indicating linear surface dispersion and a Fermi level $\sim 0.3$ eV above the band crossing. (b) ARPES images for various incident photon energies.

model, where the conductance is given by $G_{xx} \sim e^{-(T/T_0)^{-1/4}}$, suggests that the transport is dominated by 3D VRH from 100 K down to 20 K (red solid line in figure 4.3b), while at low temperature below 20 K the deviation from the fit signifies ongoing metallic conduction from the surface states, although no apparent saturation was observed for $R_{xx}$ at low temperatures (upper inset of figure 4.3a).

Figure 4.3  Temperature-dependent transport of BST. (a) Sample resistance as a function of temperature. (b) Low temperature conductance and variable-range hopping fitting. (c) Hall coefficient as a function of temperature.

This behavior is further supported with measurements of weak anti-localization (WAL)
and Shubnikov-de Haas (SdH) oscillations in the sample. The temperature-dependent low-field Hall coefficient (figure 4.3c) $R_H$ undergoes a transition in its sign from upon cooling from 300 K to 1.9 K from positive to negative, indicating a change in the dominant charge carrier from holes to electrons. A similar observation has been made in BTS\textsuperscript{57, 58}. The inset of figure 4.3c shows the Hall resistance as a function of magnetic field at a sample temperature of 1.9 K. The slope shows little difference between $R_H$ at low and high fields. The low-field Hall coefficient $R_H = -10.9 \Omega T^{-1}$ at 1.9 K provides an estimate of the electron concentration to be $1.4 \times 10^{16} \text{cm}^{-3}$, which is in the same order of magnitude as BTS\textsuperscript{57, 58}. Additionally, the Hall mobility can be calculated to be $264 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. It is believed that the low mobility of surface carriers could enhance the surface state detection due to the suppression of bulk carrier interference with quantum oscillations\textsuperscript{57, 22, 58}. This should aid in the detection of surface transport in BST crystals.

To further study the transport of the surface states, the magnetoresistance was studied by sweeping the perpendicular magnetic field at various temperatures, looking for signs of WAL. As mentioned before, WAL is a quantum correction to the classical magnetoresistance, and originates in TIs from the Berry’s phase associated with the helical surface states\textsuperscript{48, 66, 67}. The sheet magnetoresistance at different tilt angles of the magnetic field ($\theta$) reveals the feature of WAL, namely, the presence of sharp cusps around zero magnetic field\textsuperscript{48, 51, 32, 52, 54, 68}. WAL which is induced by 2D surface states is characterized by a sole dependence on the perpendicular component of the applied magnetic field, $B \sin \theta$, of the magnetoresistance. Thus, to extract the 2D surface state contribution, the 3D WAL contribution from the magnetoconductance at non-perpendicular angles can be subtracted off where

$$\Delta G_{xx}(\theta, B) = \frac{1}{R_{xx}(\theta, B)} - \frac{1}{R_{xx}(0, B)}.$$

Figure 4.4a shows traces of the sheet magnetoconductance as a function of $B \sin \theta$. The difference in conductance $\Delta G_{xx}(\theta, B)$ displays cusp-like maxima at $B = 0$ for each tilt angle and all traces follow the same curve at low magnetic fields ($\leq 0.1 T$) but they deviate from each other at higher magnetic fields, which confirms the 2D nature of the WAL effect in the sample\textsuperscript{51, 32}. Figure 4.4b shows the temperature-dependence of $\Delta G_{xx}$. As seen previously, the WAL cusps broaden and finally disappear\textsuperscript{51, 32, 54} as the temperature rises above $\sim 10 K$, due to the decrease in the phase coherent length (which is shown in figure 4.4d).
Figure 4.4  WAL in BST. (a) Magnetoconductance versus normal component of magnetic field for various orientations of incident magnetic fields. (b) Magnetoconductance at various temperatures. WAL gradually fades as temperature rises. (c) Fitting of magnetoconductance to the HLN model at 1.9 K. (d) Phase coherence length at low temperatures.

As shown previously, the quantum correction to the 2D magnetoconductance can be described by the Hikami-Larkin-Nagaoka (HLN) model\textsuperscript{46}. In the regime of strong spin-orbit coupling and low mobility, i.e. $\tau_{\phi} \ll \tau_{SO}$ and $\tau_{\phi} \ll \tau_{e}$, the conduction correction is given by

$$
\Delta G_{WAL}(B) = G(B) - G(0) \approx \alpha \frac{e^2}{2\pi^2\hbar} \left( \ln \left( \frac{B_{\phi}}{B} \right) - \psi \left( \frac{1}{2} + \frac{B_{\phi}}{B} \right) \right)
$$

(4.1)

where $\tau_{\phi}$ is the dephasing time, $\tau_{SO}$ is the spin-orbit scattering time, $\tau_{e}$ is the elastic scattering time, $\alpha$ is the WAL coefficient, $e$ is the electron charge, $\hbar$ is the reduced Planck’s constant, $\psi$ is the digamma function, and $B_{\phi} = h/4e\ell_{\phi}^2$ is a magnetic field characterized by the coherence length $\ell_{\phi} = \sqrt{D\tau_{\phi}}$ with $D$ being the diffusion constant. For the topological surface states the
value of $\alpha$ should be 0.5 for WAL. Fitting $\Delta G_{xx}$ at 1.9 K with the HLN equation yields $\alpha = 0.56$ and $\ell_\phi = 318 nm$, as shown in figure 4.4c, confirming the 2D nature of the WAL in this sample. The coherence length decreases from 318 nm to 150 nm as the temperature increases from 1.9 K to 10 K and this monotonous reduction in coherence length has also been observed in other TI systems$^{32,54}$. Using a power-law fit for figure 4.4d the relationship $\ell_\phi \sim T^{-0.44}$ is found. Theory states that for 2D systems the power law dependence should be of the form $\ell_\phi \sim T^{-1/2}$, while for 3D systems$^{69}$ the form should be $\ell_\phi \sim T^{-3/4}$. Therefore, the temperature-dependent behavior of the coherence length agrees strongly with the notion of WAL originating from the 2D surface states.

Finally, having established good evidence of the topological surface states on the surface of the BST flake, an additional experiment can be conducted to further confirm the surface states via SdH oscillations$^{26,70,71,24,72}$. For studying quantum oscillations in the nanoflake, again a magnetic field is applied perpendicular to the flake and applied current. The magnetic field dependent longitudinal resistance $R_{xx}$ shows traces of SdH oscillations in the raw data. After a direct subtraction of the smooth background, the oscillatory part of $R_{xx}$ or $\Delta R_{xx}$ displays periodic peaks and valleys with $1/B$, as shown in figure 4.5a, revealing the evident existence of a well-defined Fermi surface$^{26,71,73}$. The SdH oscillations survive up to 7 K. Using a fast Fourier transform (FFT), a single oscillation frequency can be extracted to be $f_{SdH}(T) \sim 44.9T$. For a 2D system, the SdH oscillation frequency is related directly to the Fermi surfaces cross sectional area $A_F$ in momentum space via the Onsager relation $f_{SdH} = (\hbar/4\pi^2 e)A_F$ where $A_F = \pi k_F^2$ and $k_F$ is the Fermi vector, $e$ is the electron charge, and $\hbar$ is Planck’s constant. The 2D surface carrier density $n_{2D}$ is simply related to the Fermi vector by the expression $n_{2D} = k_F^2/4\pi$, and the Fermi vector can be determined using the Onsager relation to be $k_F = 0.037 \AA^{-1}$. This leads to a carrier density of $n_{2D} = 1.1 \times 10^{12} cm^{-2}$.

If the SdH oscillations were to have come from the bulk states, the period of SdH oscillations must then be related to a 3D Fermi sphere with a radius of $k_F = 0.037 \AA^{-1}$ in momentum space and that would lead to a carrier density of $7.45 \times 10^{18} cm^{-3}$, which varies substantially from the value of $1.4 \times 10^{16} cm^{-3}$ that was obtained via Hall measurements. This reinforces the belief that SdH oscillations are originating from the 2D surface states. In figure 4.5b, the plot
shows 1/B values corresponding to the maxima (red closed circles) and minima (blue closed rectangles) of $\Delta R_{xx}$ versus the Landau level index $n$. Linear fitting of the data yields a finite intercept of 0.29 (corresponding to a Berry phase of $0.42\pi$), highlighting the topological surface states as the origin of the SdH oscillations. The discrepancy of the extrapolated values with the expected value of $0.5\pi$ from the massless Dirac fermions have been reported by several groups and the possible origin of this discrepancy is attributed to the Zeeman coupling of the spin to the magnetic field, in which a 2D quantum limit was achieved under a high magnetic field ($\sim 60T$). It has also been speculated that the deviation from the ideal linear dispersion of Dirac fermions can account for the discrepancy in the Berry phase. In the current study, the magnetoresistance measurement was performed at a maximum magnetic field of only 9 T, leading to the belief that non-ideal dispersion in the energy bands, which is also supported by ARPES, is the cause of the variance in the Berry phase. Additionally, it is also possible to extract a value of $k_F = 0.036\, \text{Å}^{-1}$ by fitting 1/B with Landau filling levels. This is in good agreement with the aforementioned SdH calculations.

The temperature-dependent amplitude of $\Delta \sigma_{xx}$ of the SdH oscillations can be described by

$$\frac{\Delta \sigma_{xx}(T)}{\Delta \sigma_{xx}(0)} = \frac{\lambda(T)}{\sinh(\lambda(T))}$$

where $\lambda(T) = 2\pi^2 k_B T m_{cycl}/\hbar e B$ where $m_{cycl}$ is the cyclotron mass, $\hbar$ is the reduced Planck’s constant, and $k_B$ is Boltzmann’s constant. It is found that $m_{cycl} \sim 0.111 m_e$ by using the best fit of the conductivity oscillation amplitude to the expression $\Delta \sigma_{xx}(T)/\Delta \sigma_{xx}(0)$ where $m_e$ is the free electron mass. The result is shown in figure 4.5c. Now, the Fermi level is described by $E_F = m_{cycl} V_F^2$ and $m_{cycl} V_F = \hbar k_F$ where $V_F$ is the Fermi velocity. These expressions yield a Fermi level of $\sim 95 meV$ above the Dirac point and a Fermi velocity of $3.9 \times 10^5 \, \text{ms}^{-1}$, lower than what was found via ARPES experiments. Previous reports on Bi$_2$Se$_3$ suggest that for samples with low carrier concentrations ($\sim 10^{17} \, \text{cm}^{-3}$), discrepancies emerge for the position of the Fermi level between ARPES and transport experiments. The discrepancy can be attributed to surface charge accumulation induced band-bending, while the lower Fermi velocity ($3.9 \times 10^5 \, \text{ms}^{-1}$) obtained from SdH oscillations when compared with ARPES ($6.4 \times 10^5 \, \text{ms}^{-1}$) is probably due to the deviations of surface states from the linear dispersion when going away
Figure 4.5  Quantum Oscillations in BST. SdH oscillations present in magnetoresistance measurements. (b) Fitting of 1/B to the Landau index. (c) SdH oscillation amplitude at low temperature for obtaining the cyclotron mass. (d) Dingle plot for calculating carrier lifetime and mean free path.

from the Dirac point$^{60}$. Finally, the transport lifetime of the surface states $\tau$ can be estimated by using the Dingle plot. Since $\Delta R/R_0 \sim [\lambda(T)/\sinh \lambda(T)] e^{-D}$, where $D = 2\pi^2 E_F/\tau e BV_F^2$, the lifetime $\tau$ can be derived from the slope in the Dingle plot by $\log[(\Delta R/R_0)B \sinh \lambda(T)] \approx [2\pi^2 E_F/\tau e V_F^2](1/B)$ (figure 4.5d). The fit provides a transport lifetime of $\sim 3.5 \times 10^{-13}s$, corresponding to a mean free path $\ell \sim 136nm$. The surface mobility $\mu_s = e\tau/m_{cycl} = e\ell/h\kappa_f$ can be estimated as $\sim 5593cm^2V^{-1}s^{-1}$, which is more than twenty times larger than the Hall mobility of $264cm^2V^{-1}s^{-1}$ from the bulk. By these calculations, the surface contribution to the total conduction can be estimated to be $\sim 57\%$. 
4.4 Conclusions

In this experiment, BST nanoflakes were mechanically exfoliated from a bulk crystal for studying their topological surface states. ARPES experiments provide direct evidence of the linear band dispersion on the surface. The high binding energy of the Dirac point as calculated from ARPES possibly originates from out-diffusion of Se during pre-annealing prior to ARPES measurements, leading to Se vacancies in the crystal. Both the WAL effect and SdH oscillations have unambiguously shown that surface transport is dominant in these flakes. Theoretical calculations predict that introducing Te into the central QL of Bi$_2$Se$_3$ to form BST can form a superior TI material that behaves like Bi$_2$Se$_3$ with a well-defined Dirac cone located inside the bulk band gap. However, finding an effective way to introduce the Te into the central QL instead of the outer two layers remains a challenge. Using elements such as Sb and Sn for doping in BST may provide an alternate way for tuning the relative position of the Fermi level and Dirac point, making BST more useful for exploring topological insulators.
CHAPTER 5. RESULTS OF A STUDY ON TRANSPORT IN CR-DOPED BI$_2$TE$_3$ THIN FILMS

5.1 Introduction

It was emphasized previously that many applications of TIs require that a surface energy gap be opened and that this can be accomplished, for instance, by inducing magnetic ordering in the material via elemental doping or, in fact, any perturbation that breaks TRS. In this experiment, we grew high-quality Cr-doped Bi$_2$Te$_3$ thin films with varying Cr concentrations on muscovite mica substrates via molecular beam epitaxy (MBE) for the purpose of studying the crystal quality and electric transport under varying temperatures and Cr concentrations. The crystal quality of the thin film surfaces were analyzed in situ using reflection high-energy electron diffraction (RHEED) and were additionally characterized after growth using an atomic force microscope (AFM) and were shown to exhibit atomically smooth terraces on the order of a micrometer. We then analyzed the thin films via energy-dispersive x-ray spectroscopy to obtain the elemental composition of undoped and doped films. Finally, a physical properties measurement system (PPMS) was used to obtain magnetoresistance and Hall transport measurements at temperatures as low as 1.9 K. At sufficient Cr coping concentration magnetic ordering of the Bi$_2$Te$_3$ films is indicated by the anomalous Hall effect below ~ 30 K. Also observed was a cross-over of the magnetoresistance from dominant weak anti-localization (WAL) behavior to dominant weak localization (WL) behavior at low temperatures as the Cr concentration is increased.
5.2 Experiment and Measurements

For this experiment, high-quality thin films of Cr-doped Bi$_2$Te$_3$ with atomically flat surfaces were grown on muscovite mica substrates. Two inch wafers of mica were cleaved using a razor blade to expose a fresh crystal surface for the films to be grown on. The cleaved mica wafers were then loaded into a high-vacuum MBE chamber with a base pressure of $\sim 10^{-10}$ Torr. High-purity bismuth, tellurium, and chromium elemental sources were then heated in the MBE growth chamber in standard effusion cells and were allowed to deposit and interact on the heated mica substrate surface. The growth is performed in a Te-rich environment to help improve the crystal quality due to the large amount of molecular Te$_2$ present in the vapor from the Te effusion cell$^{76}$. For transport measurements, films were grown to a thickness of 15 QL, giving a growth rate of $\sim 0.5QL/min$. Samples were grown with a large range of Cr-concentrations and the Cr cell temperature was adjusted between 1020 C and 1220 C. For growth, the Bi cell was kept at 520 C, the Te cell at 320 C, and the substrate temperature ranged from 245 C to 275 C. The crystal quality on the surface was studied during growth using a RHEED system that allows electrons to be incident upon the surface at a grazing angle so that they can diffract off the top few layers of atoms.

After the growth of the crystals, the surfaces were further characterized for morphology and roughness using a Digital Instruments Nanoscope IIIa AFM. The films were then analyzed for elemental composition using an Oxford Instruments Aztec energy-dispersive X-ray spectrometer (EDS) unit attached to a scanning electron microscope (FEI Quanta 250 FE-SEM) to verify the composition of undoped Bi$_2$Te$_3$ thin films and the placement and concentration of Cr in doped films. For samples grown under a Cr cell temperature below 1160 C, the calibrated flux ratios of the Cr and Bi cells had to be used in addition to EDS to infer the Cr concentration. Next, the Bi$_2$Te$_3$ thin films were etched into a standard six-terminal Hall bar geometry using reactive ion etching (RIE) in preparation for transport experiments. Ohmic contacts were made with the Hall bar etched samples using room-temperature cured silver paste and the transverse and longitudinal resistances were then measured using a Quantum Design PPMS that can sweep the magnetic field between $\pm 9T$ at temperatures as low as 1.9 K.
5.3 Results

With MBE, 15 QL films of Cr-doped Bi$_2$Te$_3$ were grown on muscovite mica via van der Waals epitaxy. During the growth, the quality of the crystal surface was monitored in situ via RHEED. The RHEED pattern from a typical Bi$_2$Te$_3$ sample is shown in figure 5.1d. The sharp streaky lines indicate an atomically flat surface and a layer-by-layer 2D growth mode where 1 quintuple layer (QL) is deposited at a time.

After growth, the films with varying Cr concentrations were characterized by EDS to check the elemental composition. Results indicate that Cr is substituting for Bi in the QL layer structure (figure 5.1e) as the atomic percent of Te present in the films remains steady around 60%, even for highly doped films. This is consistent with previous studies with Cr-doping in Sb$_2$Te$_3$ and Bi$_2$Se$_3$ where Cr substitutes on the Sb or Bi sublattices$^{77, 78}$. Therefore, the resulting compound can be expressed as Cr$_x$Bi$_{2-x}$Te$_3$. Next, the films were examined by AFM for characterization of the film surface. Figure 5.1a-c show AFM images (5µm by 5µm) from the surface of pure Bi$_2$Te$_3$ (a), low Cr concentration Cr$_{0.08}$Bi$_{1.92}$Te$_3$ (b), and high Cr concentration Cr$_{0.27}$Bi$_{1.73}$Te$_3$ (c). All have surfaces that range in height across the image of less than $\sim$5nm or 5 QL. The surfaces of the undoped samples all contained large micron sized terraces, but with one terrace covering most of the surface with smaller pockets where the coverage is incomplete or there is nucleation of the next QL, confirming the layer-by-layer growth mode via RHEED. In the low doping regime, surfaces formed triangular shaped terraces without roughing the surface relative to undoped sample. For highly doped films, the surface is rougher with no apparent terraces, but with no big peaks or valleys either with a root mean square (RMS) roughness of $\sim$1nm. The increased roughness is likely due to the competition between Bi and Cr for sites on the Bi sublattices$^{79}$. After verifying the quality and composition of the thin film, transport measurements were performed.

The Cr$_x$Bi$_{2-x}$Te$_3$ films were etched into the standard Hall bar shape using RIE and ohmic contacts were made using room temperature cured silver paste for low temperature transport measurements using a PPMS with the magnetic field perpendicular to the film surface. Figure 5.2a displays the magnetoconductivity (MC) of an undoped Bi$_2$Te$_3$ sample. The upward cusps
in MC around $B = 0$ are indicative of WAL$^{51, 48, 47, 66}$. As the magnetic field is applied and TRS is lifted, the surface carriers begin to backscatter, leading to a sharp reduction in the conductivity of the sample around $B = 0^{47, 54, 32}$. Theory suggests that doping with magnetic impurities will lead to competition with WAL and WL simultaneously$^{50, 80, 53, 49}$. For a lightly doped sample ($x = 0.08$), at 1.9 K the sample shows no sharp WAL cusp, but instead there is a broad upward cusp with a sharper downward cusp for small magnetic fields (figure 5.2b), and those features remain in a suppressed form at 2.5 K. Around 3.1 K, there is a return of the WAL cusp, but it is quickly suppressed at the temperature increases further. When the Cr concentration is further increased to $x = 0.10$, WAL is completely suppressed and a non-monotonic behavior is present up to 3.1 K (figure 5.2c) before the classical parabolic dependence of the MC appears around 4 K. Further increasing the doping concentration to $x = 0.14$, the downward cusp feature is present up until around 10 K, indicating the dominance of WL (figure 5.2d).

Recall that WAL and WL featured can be described by the HLN model$^{46}$. 

Figure 5.1  Surface morphology and crystal structure of Cr-doped Bi$_2$Te$_3$ films.  (a-c) 5 µm by 5 µm AFM images of the surface of (a) Bi$_2$Te$_3$, (b) Cr$_{0.08}$Bi$_{1.92}$Te$_3$, and (c) Cr$_{0.27}$Bi$_{1.73}$Te$_3$.  (d) RHEED pattern of film during growth.  (e) Schematic of the crystal structure.
\[ \Delta \sigma_{WAL}(B) = \sigma(B) - \sigma(0) \approx -\alpha \frac{e^2}{2\pi^2 \hbar} \left( \ln \frac{B_\phi}{B} - \psi \left( \frac{1}{2} + \frac{B_\phi}{B} \right) \right) \] (5.1)

where \( \alpha \) is the WAL coefficient, \( e \) is the electron charge \( \hbar \) is the reduced Planck’s constant, \( \psi \) is the digamma function, and \( B_\phi = \hbar/e\ell_\phi^2 \) is a magnetic field characterized by the coherence length \( \ell_\phi = \sqrt{D\tau_\phi} \) with \( D \) being the diffusion constant and \( \tau_\phi \) is the dephasing time. For the topological surface states the value of \( \alpha \) should be -0.5 for WAL. The undoped samples show WAL behavior and can be fitted well using HLN model (figure 5.2e and figure 5.2f). The resulting \( \alpha \) values range from -0.65 to -0.75 and are indicated by the black squares in figure 5.2h, near the ideal -0.5 for WAL.

Figure 5.2 MR transport of \( \text{Cr}_x\text{Bi}_{2-x}\text{Te}_3 \) films at low Cr concentration. (a-d) Magnetoconductivity for (a) \( x = 0 \), (b) \( x = 0.08 \), (c) \( x = 0.10 \), and (d) \( x = 0.14 \). (e) Fitting of (a-d) to the HLN model at 1.9 K. (f) Fitting of undoped sample to HLN model. (g) Fitting of sample with \( x = 0.14 \) to HLN model. (h) Fitting parameters \( \alpha \) in the HLN model as a function of temperature.

The resistance of the Hall channels for heavily doped films was also observed to investigate ferromagnetism in the \( \text{Cr}_x\text{Bi}_{2-x}\text{Te}_3 \) films. Not until \( x \) reaches as high as around \( x = 0.14 \) is there hysteresis in the Hall resistance. As shown in figure 5.3, \( R_{yx} \) displays hysteresis at low temperatures due to the anomalous Hall effect, showing a signature of a long-range ferro-
magnetic ordering in the thin films. The Hall resistivity in a magnetic sample is known to be 
given by \( \rho_{yx} = R_{yx} d = R_H B + \rho_{AH}(M) \), where \( d \) is the thickness of the film, \( B \) is the applied 
magnetic field in Tesla, \( M \) is the magnetization, and \( R_H \) is the ordinary Hall coefficient\(^{14, 1} \). The first term is the ordinary Hall resistivity and the second term describes the anomalous Hall 
contribution that arises from the magnetization of the material. The anomalous contribution 
can be written as a term proportional to the magnetization, \( \rho_{AH}(M) = R_A M \), with \( R_A \) as the 
anomalous Hall coefficient. The quasi-rectangular hysteresis loops of the Cr\(_x\)Bi\(_{2-x}\)Te\(_3\) films 
for \( x = 0.14, 0.27, 0.30, 0.32 \) at low temperatures is shown in figure 5.3a-d, respectively. In 
each case, the saturation Hall resistance and magnetization switching field lessen to suppress 
the hysteresis as the temperature increases. In figure 5.3e the temperature-dependent Hall 
resistance \( R_{yx} \) of Cr\(_x\)Bi\(_{2-x}\)Te\(_3\) films at zero magnetic field are shown. The overall resistance 
increases with increasing Cr concentration, as expected, with the effect being damped as the 
temperature increases for these highly doped Cr samples. However, \( R_{yx} \) does not completely 
vanish in the measured temperature range (figures 5.3a-e). A similar behavior was reported in 
Mn\(_x\)Bi\(_{2-x}\)Te\(_3\) thin films grown on GaAs, and the remaining hysteresis behavior is ascribed to 
the defect and impurity states from the mica substrate and so an alternative approach is need 
to estimate the Curie temperature \( T_C \) in each film. Using Arrott plots, \( R^2_{yx} \) is plotted against 
\( B/R_{yx} \) for each temperature and the extrapolated intercept along the \( R_{yx} \) axis is proportional 
to the saturation magnetization. The inferred temperature at which the \( R_{yx} \) intercept goes to 
zero is the Curie temperature \( T_C \). The extracted values for the Curie temperature at different 
doping concentrations is shown in figure 5.3g.

The carrier concentrations of the samples can be extracted (figure 5.3f) by determining the 
slope of the Hall resistance at large magnetic fields where the response is linear, as the slope 
is characterized by the Hall coefficient \( R_H \) and \( R_H \) is related to the carrier concentration \( n \) by 
\( |R_H| = 1/en \), where \( e \) is the electron charge. For all values of Cr concentration, the sign of the 
Hall slope indicated n-type conduction. Figure 5.3f shows that the sheet carrier concentration 
as a function of Cr concentration increases with increasing temperatures below 10K. For high 
Cr concentration samples (\( x \sim 0.30 \)) band bending or an inhomogeneous chemical potential 
may indicate why the bulk carrier concentration is as high as\(^{81, 82} \) \( 10^{14} \sim 10^{15} cm^{-2} \).
Figure 5.3  Hall transport of Cr$_x$Bi$_{2-x}$Te$_3$ films. (a-d) Hall resistance at various temperatures for (a) $x = 0.14$, (b) $x = 0.27$, (c) $x = 0.30$, and (d) $x = 0.32$. (e) Saturation anomalous Hall resistance versus temperature. (f) Two-dimensional carrier density from Hall measurements. (g) Curie temperature as a function of Cr concentration.

It was seen earlier that the MC is dominated by WL once the Cr concentration is high enough for ferromagnetic ordering ($x = 0.14$). Figure 5.4 shows the MC for the high Cr concentrations $x = 0.27$ (a), $x = 0.30$ (b), and $x = 0.32$ (c). As with the Hall data, the hysteresis behavior is due to the ferromagnetism which is suppressed as the temperature increases and approaches the Curie temperature$^{83, 79, 40}$. All plots indicate qualitatively WL behavior. The two minima in the MC at low temperatures indicate the coercivity of the sample and, consistent with the anomalous Hall data, the coercive force varies little with Cr concentration at high concentrations.
Figure 5.4 MC transport of Cr$_x$Bi$_{2-x}$Te$_3$ films at high Cr concentration. Magnetococonductivity for (a) x = 0.27, (b) x = 0.30, and (c) x = 0.32. Films show WL behavior with hysteresis.

5.4 Conclusion

This work was completed to study the effects of Cr doping in thin films of the TI material Bi$_2$Te$_3$. High quality Cr-doped Bi$_2$Te$_3$ films with atomically flat surfaces can be grown on mica. Cr atoms in doped samples occupy Bi lattice sites and lead to an overall roughening of the crystal surface without having much of an effect on the height range of the surface. WAL was found in the undoped sample, and a transition occurred as the Cr concentration grew due to the disordering effects of Cr and a WL effect began to dominate over WAL in the light doping regime ($x \leq 0.14$). For Cr$_x$Bi$_{2-x}$Te$_3$ films with $x \geq 0.14$, ferromagnetic ordering is indicated by a non-zero magnetization via the anomalous Hall effect. For highly doped samples the Curie temperature was as high as $\sim 30K$. The large carrier concentrations in the heavily doped ferromagnetic films indicate that the origin of ferromagnetism is likely the van Vleck mechanism and is not mediated by Dirac fermions.
CHAPTER 6. CONCLUSION AND FUTURE WORK

Topological insulators are a recently discovered class of materials that differ from ordinary insulators due to a band inversion brought about by strong spin-orbit coupling. This makes its band structure topologically distinct from ordinary insulators and leads to the creation of conducting surface states at the interface of a topological insulator and an ordinary insulator (or air/vacuum) where the topology of the band structure must change. Due to the topological origin of the conducting surface states, the form of the surface dispersion is robust and a surface energy gap will not open if there are perturbations in the crystal that do not break time-reversal symmetry. The band structure of the surface is described by an odd number of linearly dispersed Dirac-cones which contain spin-polarized states where the spin of a carrier is determined uniquely by the direction of the wavevector $\vec{k}$. The topological protection of the conducting surface states together with their spin-polarized nature force a suppression in backscattering on the surface and allow for near-dissipationless spin-currents to flow along the surface.

The surface states can form a surface energy gap in the presence of perturbations that break time-reversal symmetry such as applying a magnetic field normal to the surface or by inducing a net out-of-surface magnetization in the material. Such perturbations will create an energy splitting between spin-up and spin-down bands on the surface and will allow for surface backscattering. The opening of the surface energy gap allows not only for the possibility of switching the surface between conducting and insulating states, but is important for observing several interesting phenomena such as the anomalous quantum Hall state and a related magnetoelectric coupling which allow an applied electric field to generate a magnetic dipole and an applied magnetic field to induce an electric dipole. However, experimental verification and manipulation of the conducting surface states has been challenging due to the small bulk band
gaps (\(\sim 300\text{meV}\) or less) and impurities in grown topological insulator crystals which cause the bulk conduction to obscure the surface conduction properties. The issues with bulk conduction can be alleviated using methods such as electrical gating, elemental doping, or composition tuning in ternary compounds to lower the bulk carrier density. Additionally, nanostructures, where the volume to surface area ratio is reduced, can be used to lower the overall transport contribution from the bulk.

Several experimental methods have also proven useful in verifying the predicted nature of the surface states. The first experimental verification of three-dimensional topological insulators come from angle-resolved photoemission spectroscopy studies where high energy (x-ray) photons are incident upon a sample and the energy and momentum distribution of ejected electrons is collected to reconstruct the band structure of the material. Oscillations in the magnetoconductance via the Aharonov-Bohm effect and especially Shubnikov-de Haas oscillations are now regularly used to confirm the conducting nature of the surface states and to extract many properties such as the carrier lifetime and phase coherence length. The coherence of surface carriers that leads to the lowered resistance in the material due to weak anti-localization can be destroyed by applying a magnetic field. Fitting the magnetoconductivity data to the two-dimensional Hikami-Larkin-Nagaoka model describing weak anti-localization is often used in order to confirm the existence of the two-dimensional surface states from transport experiments.

In this work, the results from the characterization of nanoflakes of the topological insulator Bi\(_2\)Se\(_2\)Te and thin films of the Cr-doped topological insulator Bi\(_2\)Te\(_3\) are presented. The Bi\(_2\)Se\(_2\)Te nanoflakes were first grown as part of a bulk crystal and were mechanically exfoliated from the bulk crystal after verifying the composition along the axis of the ingot. Transmission electron microscopy and x-ray diffraction experiments were then used to investigate the crystal properties. It was found that the crystal structure is similar to the structure seen in Bi\(_2\)Se\(_3\) and other Sb and Bi based topological insulators, but deviates from the Bi\(_2\)Se\(_3\) quintuple layer structure by disordered occupation of Te and Se on the two outer layers of the quintuple layer structure. The non-stoichiometric formula for the nanoflake used in transport experiments was Bi\(_2\)Se\(_{1.88}\)Te\(_{1.12}\). Angle-resolved photoemission spectroscopy was performed and shows the predicted linear dispersion from the surface states and an estimated value of the Fermi level to
be \sim 0.3eV above the Dirac point with a Fermi wavevector of 0.07\,\AA^{-1}.

Low temperature transport measurements were made using a physical properties measurement system which allowed for the measurement of resistance from room temperature down to 1.9 K and for magnetoresistance and Hall measurements at magnetic fields as high as 9 T. Temperature-dependent resistance measurements show insulating behavior throughout most of the temperature range with metallic-like conduction below \sim 20K and an activation energy of \sim 100\,meV. Magnetococonductance measurements at low temperatures show the two-dimensional weak anti-localization characteristic predicted by the Hikami-Larkin-Nagaoka model gradually weakens as the temperature is brought above \sim 10K, suggesting the strong influence of the conducting surface states at these low temperatures to the overall transport. Shubnikov-de Haas oscillations were discovered in the magnetoresistance below 7 K and were used to verify the existence of the surface states and to extract many surface carrier properties such as the cyclotron mass (\sim 0.111m_e where \emph{m}_e is the electron rest mass) from the oscillation amplitude and the carrier lifetime of \sim 3.5 \times 10^{-13}\,s from the Dingle plot. From this the surface mobility was found to be more than twenty times higher than the bulk mobility from Hall measurements. Hall measurement allow for an estimate of the carrier density at 1.9 K to be 1.4 \times 10^{16}\,cm^{-3} with a Hall mobility of 264\,cm^2V^{-1}s^{-1}. The transport measurements show that at low temperatures (near 1.9 K) the surface contribution to the total conduction reaches around 57 percent. The experiments verify the conducting surface states in the topological insulator Bi$_2$Se$_2$Te and shows the promise in using nanostructures to limit the bulk conduction for studying the surface transport properties in this material system.

In addition to the experiments done on Bi$_2$Se$_2$Te, thin films (\sim 15\,nm) of the topological insulator Bi$_2$Te$_3$ were created with varying amounts of Cr impurities using molecular beam epitaxy on a mica substrate. During growth the samples were monitored via reflection high-energy electron diffraction and were shown to have a crystalline structure with a layer-by-layer growth mode. Atomic force microscope images show atomically flat surfaces with terraces with a height of \sim 1\,nm, corresponding to one quintuple layer. The surface roughens with the addition of Cr into the lattice, while still keeping the range of height of the surface within 5 nm. Energy-dispersive x-ray spectroscopy was used to verify the composition of the Cr-doped Bi$_2$Te$_3$
films and it was found that Cr occupies sites on the Bi sublattices, allowing for the films to be characterized by formula Cr$_x$Bi$_{2-x}$Te$_3$. The films were additionally characterized via transport experiments with a physical properties measurement system. Magnetoconductance measurements show that undoped films show weak anti-localization behavior at temperatures near 1.9 K. As the Cr concentration increases the films begin to display competition between weak anti-localization (characterized by increased resistance upon applying a magnetic field) and weak localization (characterized by lowered resistance upon applying a magnetic field). With high Cr doping, weak anti-localization is completely suppressed and the coherent backscattering of carriers from disorder due to weak localization, is dominant. The Hall resistance in the Cr$_x$Bi$_{2-x}$Te$_3$ samples begin to show hysteresis when $x \geq 0.14$, suggesting ferromagnetic ordering. The hysteresis can also be found in the magnetoresistance measurements at these high Cr concentrations. The Curie temperature was estimated by finding the lowest temperature for which the hysteresis in the Hall data would disappear and by using Arrott plots. The methods give similar results and the data is consistent with other reports of the Curie temperature rising linearly with increasing Cr concentration. In our study, the Curie temperature reached around 30 K in the compound Cr$_{0.32}$Bi$_{1.68}$Te$_3$. The transport data from this study suggests that adding Cr to Bi$_2$Te$_3$ thin films leads to ferromagnetic ordering and that the conducting surface states are lost due to the addition of Cr into the lattice from a suppression of weak anti-localization. Additionally, the Cr content of the films leads to disorder and weak localization will become more prominent as the Cr concentration increases.

Future work in TIs will continue to focus on providing materials of high crystal quality and more insulating behavior while continuing to develop experimental procedures for easily studying and manipulating the surface transport. In studying TIs with an induced surface gap, future work should set out to better understand the effects of magnetic dopants on the materials band structure and to better understand the best dopant materials to use to induce strong magnetism at high temperatures and low concentration while not substantially altering the band structure or carrier density. More work is needed to understand the different effects that a particular magnetic dopant may have on different TI materials. Once the effects of broken TRS induced by magnetic effects is more thoroughly studied, researchers will develop a
better understanding of the mechanisms by which magnetic ordering occurs in these materials, which could aid in choosing the most promising dopants for TI materials and devices produced from them.
APPENDIX
ADDITIONAL MATERIAL

Published Papers


Book Chapters

BIBLIOGRAPHY


