IMPACT OF POINT DEFECTS ON ELECTRONIC PROPERTIES OF TOPOLOGICAL MATERIALS

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A dissertation submitted to the
School of Graduate Studies
Rutgers, The State University of New Jersey
In partial fulfillment of the requirements
For the degree of
Doctor of Philosophy
Graduate Program in Physics and Astronomy
Written under the direction of
Weida Wu
And approved by

New Brunswick, New Jersey
October, 2019
Topological insulators and topological Weyl semimetals are both novel classes of quantum materials. They are characterized by the surface states arising from the nontrivial topology of band structure. The surface state of topological insulators exists in the band gap, which originates from the band inversion due to the strong spin-orbit interaction. The topological Weyl semimetals are characterized by the surface Fermi arcs that connects the projections of two Weyl nodes of opposite chiralities and unusual magnetotransport properties induced by the chiral anomaly. These topological materials not only introduce novel fundamental physics concepts and properties, but also provide a new route to the development of technological applications of electronics, spintronics and topological quantum computation. Defects and impurities are inevitably present in all functional materials including topological materials. An important theme in the research of topological materials is to investigate and control defects. The goal of this doctoral thesis is to address the impact of point defects on
the electronic properties of topological materials from several different perspectives.

First, we present the experimental studies on the topological insulator Bi$_2$Se$_3$ single crystals and thin films. The prominent native defects in Bi$_2$Se$_3$ single crystals are clearly identified. In particular, Se vacancies and Se interstitial defects are responsible for the spatial fluctuation and the bulk conduction. Through the optimization of synthesis process, the formation of native defects is effectively suppressed in the Bi$_2$Se$_3$ single crystal sample, which is approaching the intrinsic limit with the Fermi level inside the band gap. We also investigate the long-lasting p-type doping problem in Bi$_2$Se$_3$ thin films. We find that the obstacles are the excess n-type defects from the interface between sample and substrate and from the air exposure. By properly protecting the surface of thin films and applying buffer layer, we have achieved p-type Bi$_2$Se$_3$ thin films via compensation doping with calcium.

Next, we study the topological phase transition in (Bi$_{1-x}$In$_x$)$_2$Se$_3$. We present compelling microscopic evidence of an inhomogeneous topological phase transition in this system, which is characterized by non-uniform spatial distributions of local band gap and topological surface states. The nanoscale inhomogeneity originates from effective suppression of local spin-orbit coupling and band topology by In defects. Our observations demonstrate that strong disorders can play a significant role in the topological phase transition.

Then we investigate the distributions of electronic defect states of magnetic dopants vanadium(V) and chromium(Cr) in the topological insulator (Bi,Sb)$_2$Te$_3$, which is the parent compound to achieve the quantum anomalous Hall effect. The spectroscopic imaging shows very diverse distributions of local defect states of V and Cr. These unique spectroscopic features of the two dopants serve as electronic fingerprints to study the Cr/V-codoped topological insulator thin films.

Finally we study the type-II topological Weyl semimetal WTe$_2$. We directly visualize the quasiparticle interference patterns of surface states emerging around point defects via scanning tunneling spectroscopy. The spin-preserved joint density of state
maps are computed via density functional theory calculations. The good agreement between the calculations and the experiments provides solid evidence of the presence of surface states on the type-II topological Weyl semimetal WTe$_2$. 
Acknowledgments

First and foremost, I would like to extend my deepest gratitude to my graduate advisor Professor Weida Wu for his commitment to both my work and my career; for his patience when teaching me all the experimental and theoretical details; for his guidance that helps me transit from a student to a professional and independent researcher; for his encouragement when I was struggled and frustrated and for his faith in my abilities. I was very lucky to work with him on all those interesting physics problems.

All my works involve closely inter-group collaborations. Professor Sang-Wook Cheong’s group at Rutgers, Professor Yew San Hor’s group at Missouri University of Science and Technology and Professor Joseph Checkelsky’s group at MIT provided us high-quality single crystal samples. We also obtained high-quality thin film samples from Professor Seongshik Oh’s group at Rutgers, Professor Cui-Zu Chang’s group at Penn State and Professor Ke He’s group at Tsinghua. Professor David Vanderbilt’s group at Rutgers, Professor Shengbai Zhang’s group at RPI and Professor Alexey Soluyanov’s group at ETH Zürich helped us understand and interpret experimental findings accurately with theoretical calculations and simulations. We also collaborated with Professor L. Andrew Wray’s group on a project combining STM and ARPES measurements. Herein I would like to sincerely acknowledge them.

My time at Rutgers would have been much less productive if I had not got support from my labmates. I especially thank Jixia Dai for the lab training I received when I initially joined the group. He was always very patient and supportive even when I made mistakes. I also thank all my labmates: Chen Chen, Wenbo Wang, Paul Sess, Zengle Huang, Wenbo Ge, Ying Liu, Yanan Geng, Zheng Ju for helpful
discussions as well as a friendly and inspiring environment in our lab.

I also enjoyed and benefited a lot from the discussions with fellow graduate students, postdocs and visitors at Rutgers, including but not limited to Kai Du, Xiaochen Fang, Bin Gao, Huijie Guan, Qiang Han, Rongwei Hu, Feiting Huang, Deepti Jain, Jae Wook Kim, Sean Kong, Seong Joon Lim, Jianpeng Liu, Jinhai Mao, Jisoo Moon, Maryam Salehi, Ying Sun, Xueyun Wang, Yazhong Wang, Fangdi Wen, Shangfei Wu, Wenhu Xu, Xianghan Xu, Mai Ye, Meng Ye, Weilu Zhang, Wenyuan Zhang, Xiaodong Zhou. Of course, this list is far from being complete.

I would also like to thank my college mates and friends who also pursue Ph.D., including Dai Bin, Tong Gao, Xingfeng He, Panyu Hou, Jiapeng Liu, Nan Jiang, Xiaoyu Ma, Tiancong Wang, Haoxiang Yang, Yiquan Zou and Xiaoyang Zhao. Their supports remind me that I am not alone along the journey.

Last and most importantly, I would like to acknowledge my family for their love and support. To my wife Yuqi Liu, who never complained my late nights and long weekends in the lab. To my mother Liyan Bai and my father Baogui Zhang, who encouraged me to pursue physics and selflessly support my life in the US.
Dedication

To my dear parents Baogui Zhang and Liyan Bai,
my beloved wife Yuqi Liu
and my cute dog Curie
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Chapter 1

Introduction

Topological materials belong to a wider range of types of matter which are rooted in quantum mechanics. Examples of such quantum materials include superconductors, graphene, topological insulators, topological semimetals, quantum spin liquids and spin ices [1]. Electrons in this class of matters cannot be viewed as independent particles because of strong interactions which give rise to collective excitations known as quasiparticles. In these materials, quantum mechanical effect plays a fundamental role in altering properties of the materials from a classical description. The properties of quantum materials can be understood in different aspects, such as symmetry, topology and entanglement. For instance, one can classify a physical system by the symmetry it obeys or breaks, which is closely related to the fundamental laws of nature. Famous examples are magnetism and superconductivity. The former property originates from the spontaneous breaking time reversal symmetry (TRS), while the ground states of the latter systems spontaneously break the U(1) gauge symmetry [2]. However, there are known examples that the states of matter cannot be explained by spontaneous symmetry breaking such as spin liquids [3]. Later it became clear that the concept of topology plays a central role in these phases, which is beyond symmetry description[4].

In this chapter, I will briefly review theoretical developments and experimental discoveries of topologically ordered materials, including integer quantum Hall insulators, quantum spin Hall insulators, 3D topological insulators, topological semimetals and quantum anomalous Hall insulators. In addition, the impact of point defects on the physical properties of such materials will also be addressed. In-depth discussions
can be found in Refs. [5, 6, 7, 8, 9, 10, 11].

1.1 Topological band theory

1.1.1 Insulating states

The development of band theory is one of successes of quantum mechanics in describing the states of electrons in condensed matter. When the two assumptions, the single particle approximation and the translational symmetry of the crystal, are satisfied, the band theory classifies the states of electrons in terms of crystal momentum $\mathbf{k}$ defined in a periodic Brillouin zone. The periodic Bloch states $|u_m(\mathbf{k})\rangle$, defined in a unit cell of crystal, are eigenstates of the Bloch Hamiltonian $H(\mathbf{k})$ of the system. The eigenvalues $E_m(\mathbf{k})$ represent the energies of band that collectively form the band structure[12].

The schematic band structure of a well-known insulating state, atomic insulator, is shown in Figs 1.1(a-b). An energy gap separates the fully occupied valence band and the unoccupied conduction band with the Fermi energy ($E_F$) lying within the gap. Generically, one can classify crystalline solids as insulators or conductors with the band theory by the existence of an energy gap at $E_F$. Although the atomic insulators such as inert gas have a much larger gap (10 eV-20 eV) than semiconductors (1 eV-10 eV), they still belong to the same topological phase, since their Hamiltonians can be deformed adiabatically to each other without closing the gap. However, not all the insulators are topologically equivalent to the atomic insulators. For example, the integer quantum Hall state which will be introduced next is actually not topologically equivalent to the conventional insulating states.

1.1.2 Integer Quantum Hall Effect

Integer quantum Hall effect is a quantized version of ordinary Hall effect, which was discovered by Hall in 1879 [13]. The ordinary Hall effect describes a production
Figure 1.1: Conventional insulating state and integer quantum Hall state (IQHS). (a-b) The atomic insulator and its band structure. (c) A semi-classical model of the IQHS: the cyclotron motion of electrons. (d) The band structure of IQHS is quantized to form Landau levels. The figures are adapted from Ref. [5]

of voltage (Hall voltage) transverse to the electric current in a conductor when a magnetic field is applied perpendicular to the direction of the current. In the presence of the magnetic field, the charge carriers experience a Lorenz force, which deflect their motion. The transverse motion of charge carriers causes charge accumulation at the side surfaces of the conductor, which creates an electric field that cancels the Lorenz force on the charges, so a steady transverse Hall voltage is established as long as the longitudinal current persists. Assuming the charge carriers are electrons, the Hall conductivity $\sigma_H$ is,

$$\sigma_H = \frac{j_x}{E_y} = -\frac{B}{ne},$$

which indicates $\sigma_H$ is proportional to the magnetic field $B$ and inverse of charge density of electrons $ne$.

In 1980, von Klitzing discovered the integer quantum Hall effect in two-dimensional electron gas (2DEG) when the 2DEG is subjected to a very low temperature and a strong magnetic field [14]. The originally continuous energy spectrum of electrons
degenerates to Landau levels,
\[ E_m = h\omega_c (m + \frac{1}{2}) \]  (1.2)
where \( \omega_c \) is the cyclotron frequency. If \( E_F \) lies between two Landau levels, the longitudinal conductivity vanishes as illustrated in Figs. 1.1(c-d), which indicates an insulating state in the bulk. Meanwhile, the Hall conductivity takes quantized values,
\[ \sigma_{xy} = n \frac{e^2}{h} \]  (1.3)
where \( n \) is the number of fully occupied Landau bands below \( E_F \).

The difference between the integer Quantum Hall (IQH) states and ordinary band insulators like atomic insulators was first recognized in a ground-breaking theoretical work performed by Thouless, Kohmoto, Nightingale and den Nijs (TKNN) [15]. They showed that the \( k \)-space of this state can be mapped to a Hilbert space that is topologically distinct from that of a ordinary insulator. The topological inequivalence means that the Hamiltonian of one gapped system cannot be adiabatically transformed to another without closing the gap. The topology can be specified by the TKNN invariant, which is related to the Berry phase. In the next section, the concept of the Berry phase will be briefly introduced.

### 1.1.3 Berry phase and TKNN invariant

Assume \( \mathbf{R}(t) \) is a set of time-dependent parameters in the form a vector of a Hamiltonian \( H [\mathbf{R}(t)] \) whose eigenstate is \( |n(\mathbf{R})\rangle \) and eigenvalue is \( \varepsilon_n(\mathbf{R}) \). If \( \mathbf{R}(t) \) changes adiabatically along a path \( C \), the general solution of the time-dependent Schrodinger equation of \( H [\mathbf{R}(t)] \) can be solved as,
\[ |\phi_n(t)\rangle = \exp (i\gamma_n(t)) \cdot \exp \left( -\frac{i}{\hbar} \int_0^t \varepsilon_n(\mathbf{R}(t')) \, dt' \right) \cdot |n(\mathbf{R})\rangle. \]  (1.4)
In this formula, the first exponential term comes from a quantum-mechanics phase accumulated along the time revolution, while the second term is a trivial dynamic
term. In Eq. 1.4, the geometric phase $\gamma_n(t)$ is defined as the Berry phase along the path,

$$
\gamma_n(t) = \int_0^t dt' \cdot \dot{\mathbf{R}}(t') \cdot i\langle n(\mathbf{R})|\nabla_{\mathbf{R}}|n(\mathbf{R})\rangle = \int_{\mathbf{R}_0}^{\mathbf{R}(t)} d\mathbf{R} \cdot i\langle n(\mathbf{R})|\nabla_{\mathbf{R}}|n(\mathbf{R})\rangle. \quad (1.5)
$$

We define the integrant as the Berry connection

$$
\mathbf{A}(\mathbf{R}) = i\langle n(\mathbf{R})|\nabla_{\mathbf{R}}|n(\mathbf{R})\rangle \quad (1.6)
$$

and the Berry curvature as the curl of the Berry connection,

$$
\Omega_n(\mathbf{R}) = \nabla_{\mathbf{R}} \times \mathbf{A}(\mathbf{R}). \quad (1.7)
$$

When $\mathbf{R}$ moves along a closed loop $C$ from $t = 0$ back to the initial position at $t = T$, i.e. $\mathbf{R}(T) = \mathbf{R}_0$, the Berry phase of the closed loop becomes

$$
\gamma_n(C) = \oint_C \mathbf{A}(\mathbf{R}) \cdot d\mathbf{R} = \int_S \Omega_n(\mathbf{R}) \cdot d\mathbf{S} \quad (1.8)
$$

which indicates that the Berry phase equals area integral of the Berry curvature on a surface enclosed by the closed loop $C$. In general, the Berry connection and Berry phase is gauge-dependent, but for a closed path, they are gauge invariant. In this sense, the Berry curvature, the Berry connection and the Berry phase in the parameter space of $\mathbf{R}$ are analogous to the magnetic field, the vector potential and the magnetic flux in electromagnetism.

The TKNN invariant of quantum Hall states can be derived if one apply the idea of Berry phase to the Bloch bands, where the crystal momentum $\mathbf{k}$ is a well-defined parameter. The Berry connection defined in Eq. 1.6 is written for the Bloch states as

$$
\mathbf{A}_n(\mathbf{k}) = i\langle u_{nk}|\nabla_{\mathbf{k}}|u_{nk}\rangle \quad (1.9)
$$

so the Berry phase of the $n$th band over the Brioulline zone is

$$
\gamma_n[BZ] = \oint_{BZ} d\mathbf{S} \cdot \gamma_n(\mathbf{k}). \quad (1.10)
$$
Now let’s consider the Hamiltonian in the presence of electromagnetic field. The semi-classical equations of motion are modified as

\[
\begin{align*}
\dot{r} &= \nabla_q \varepsilon - \dot{p} \times \Omega(q) \\
\dot{p} &= -eE - e \dot{r} \times B
\end{align*}
\]

(1.11)

Given that the magnetic field is along \(z\) direction and the current density is defined as

\[
j = -e \sum_n \int \frac{dk}{(2\pi)^2} \hat{r}_n \cdot f(k)
\]

(1.12)

where \(f(k)\) is the Fermi distribution function, the Hall conductivity can be solved:

\[
\sigma_{xy} \equiv \frac{j_y}{E_x} = \frac{e^2}{2\pi \hbar} \cdot \sum_{\text{filled } n} \oint_{BZ} dk_x dk_y \Omega_{k_x,k_y} = \frac{e^2}{2\pi \hbar} \cdot \sum_{\text{filled } n} \gamma_n [BZ]
\]

(1.13)

The single-value nature of the wave function in the Brillouin zone guarantees that the phase factor in its exponent, i.e. the Berry phase \(\gamma_n\) must be an integer multiple of \(2\pi\) and hence the Hall conductivity reduces to

\[
\sigma_{xy} = \nu \frac{e^2}{h} \quad (\nu \in Z).
\]

(1.14)

The integer \(\nu\) is called TKNN invariant or Chern number, and it defines the topological class of the IQH state, so the systems with different Chern numbers belongs to different topological classes. In this sense, the IQH insulator can be regarded as the first known topological insulator.

1.1.4 Gapless edge states

It is not intuitively straightforward that the Hall conductivity is nonzero while the system is in an insulating state. The Hall conductivity actually results from the gapless edge states at the boundary of the IQH system. In a semiclassical picture, it can be understood in terms of the skipping motion of cyclotron on the edge, as shown in Fig. 1.2. These edge states are chiral in a sense that they propagate only in one direction only the edge, and hence they are insensitive to disorders because there are no corresponding states available for backscattering.
The presence of such chiral edge states is deeply related to the topological classification. The integer quantum Hall insulators and the vacuum have different topological invariants, i.e. $\gamma_{[\text{vac}]} = 0$ and $\gamma_{[\text{IQH}]} > 0$. Since they both maintain finite gaps in the bulk, and they cannot smoothly deform to each other without closing the gap, the gap at the interface must close, which results in a gapless excitation confined to the interface. The different of Chern numbers $\gamma_{\text{QHE}}$ gives the number of chiral edge modes. The quantized values of IQHE can be experimentally determined with a very high precision, which provides a precise value of fundamental constants (e.g. fine structure constant).

![Figure 1.2](image1.png)

Figure 1.2: The chiral edge modes at the interface between a quantum Hall state and vacuum. Left: The skipping cyclotron orbits in the semiclassical picture. Right: The electronic structure of a semi-infinite interface described by the Haldane model. A gapless edge state connects the conduction band and the valence band. Adapted from Ref. [5]

### 1.2 Quantum Spin Hall Insulators

#### 1.2.1 Quantum spin Hall effect and $Z_2$ topology

To realize the IQHE, the TRS of the system needs to be broken in the presence of external magnetic field. Haldane theoretically proposed a model the quantum Hall state in zero net magnetic field in the honeycomb lattice. The nontrivial topology
results from the periodic magnetic flux, so this system still breaks the TRS [16]. Therefore, no Chern insulators with nonzero TKNN invariant can be achieved as long as the TRS is persevered. In 2005 Kane and Mele first proposed that the spin-orbit coupling (SOC) also allows a different topological class of insulators without breaking the TRS[17]. Such insulating state is called quantum spin Hall (QSH) state, which is also known as two-dimensional topological insulator. The authors further show that this phase is associated with a $Z_2$ topological invariant, which distinguishes it from an ordinary insulator.

To understand this new topological class, it is of importance to examine the role of TRS. The Block Hamiltonian of a time reversal invariant system must satisfy

$$\Theta H(k)\Theta^{-1} = H(-k)$$

(1.15)

where the time reversal operator of a spin 1/2 particle has the form of $\Theta = -is_y K$. According to the Kramer’s Theorem, the eigenstates are at least twofold degenerate at time reversal invariant momenta (TRIM) in the reciprocal space. The classification of time reversal invariant Hamiltonian can be done with the help of bulk-surface correspondence. Depending on the details of the Hamiltonian on the edge, a system may or may not present the states that bound to the edge. If there are edge states, the Kramer’s theorem guarantees that they are two-fold degenerate at TRIM. The SOC will generally lift the spin degeneracy away from TRIM. There are two ways that the edges states connect two different TRIM. Fig. 1.3(a) shows that they are connected in pairs, in which case the states can be eliminated by pushing the edge states out of the gap. Besides, between $k_x = 0$ and $k_x = \pi/a$ they cross the Fermi level even number of times. In contrast, Fig. 1.3(b) shows a case where the edge states cross $E_F$ odd number of times and they are topologically protected in the sense that they cannot be eliminated without closing the gap. The bulk-surface correspondence associate the number of a Kramer pair of edge modes intersecting $E_F$ to the change of $Z_2$ invariant across the interface.
Figure 1.3: Energy-momentum dispersion between two boundary TRIM points: (a) The number of surface states crossing $E_F$ is even; (b) The number of surface states crossing $E_F$ is odd. An odd number of crossings corresponds to topologically protected metallic boundary states.

The quantum spin Hall state was first predicted to exist in graphene[18]. Subsequently, it was proposed in HgTe/CdTe quantum well heterostructure and was then successfully observed[19].

### 1.2.2 Graphene

Graphene is an interesting material. In the absence of the SOC, its conduction band and valence band touches at $K$ and $K'$ of the Brillouin zone. The low-energy excitation near the touching points behaves like massless Dirac fermions. The corresponding Bloch Hamiltonian is,

$$H(q) = \hbar v_F \mathbf{p} \cdot \mathbf{\sigma}. \quad (1.16)$$

In 2005, Mele and Kane [18] proposed that SOC introduces a new mass term $H_{SOC} = \hbar \frac{4m^2c^2}{\hbar c}[\nabla V \times \mathbf{p}] \cdot \mathbf{\sigma}$. As the $H_{SOC}$ commutes with the spin operator $S_z$, it can be decoupled to two independent Hamiltonians with up and down spins. The result is simply two copies of aforementioned Haldane models. The SOC term does not break the TRS because the time reversal operation maps the two copies to each other. The spin-up channel and spin-down channel propagates in the opposite directions. Thus
the Hall conductivity $\sigma_{xy}$ is zero, but the spin conductivity is quantized. Since it is two copies of quantum Hall states, the gapless modes must exist on the boundary of QSH insulator, as shown in Fig. 1.4. The pair of two chiral edge modes are known as the helical edge mode.

![Figure 1.4: Edge states in the quantum spin Hall insulator (QSHI). (a) The interface between a QSHI and an ordinary insulator. (b) The energy-momentum dispersions of two edge modes showing that up and down spins propagate in the opposite directions.](image)

Note that the helical edge states in graphene are robust against strong disorder as long as the system is time reversal invariant. In contrast, the edge states of ordinary insulators, if any, are fragile in the presence of weak disorder, because they have up and down spins propagating in both directions.

Since the SOC is proportional to $Z^4$ (here $Z$ represents atomic number), the SOC in carbon atoms is very weak. The band gap opened due to SOC in graphene is only on the order of 1 $\mu$eV, which makes the experimental observation of QSH effect extremely difficult. Better solutions to this issue lie in materials with a strong SOC, usually made from heavy elements.

**1.2.3 HgTe/CdTe quantum well structure**

Hg$_x$Cd$_{1-x}$Te is a family of semiconductors with strong SOC. The band structure of CdTe resembles those of the ordinary insulators where the valance band has a $p$-type
symmetry and the conduction band has a s-type symmetry. The strong SOC in HgTe causes an inverted band structure, i.e. the p levels rising above the s levels. Bernevig, Hughes and Zhang (BHZ) [20] thus proposed a quantum well structure where HgTe is sandwiched by CdTe layers, as shown in Fig 1.5(a). Intrinsically, the bulk of HgTe is a zero-gap semiconductors, which is not qualified as a good insulator. But sandwiching it with CdTe, the in-plane lattice constant is sightly enlarged and consequently a gap is open. When the thickness of HgTe layer satisfies $d > d_c = 6.35$ nm, the bands inversion and the helical edge modes occurs. Accordingly, the conductance is quantized to be $2e^2/h$. One can tune the thickness of HgTe layer to achieve a topological phase transition from a normal insulator ($Z_2 = 0$, $d < d_c$) to a 2D topological insulator ($Z_2 = 1$, $d > d_c$). Within one year of the theoretical proposal of HgTe/CdTe structure, König et al. from Würzburg successfully realized the QSHS experimentally [19]. By tuning the gate voltage to control the chemical potential, they observed the quantization of conductance of edge states $2e^2/h$ through transport experiment at $T = 30$ mK, as shown in Fig. 1.5(b). This experiment convincingly confirms the presence of helical edge states of QSH insulators.

1.3 3D Topological Insulators

Given that the IQHE and QSHE are both confined in two dimensions, it is natural to ask if the idea of topological classification can be generalized to three dimensions (3D). Soon after the proposal of quantum spin Hall insulator, three groups independently discovered that this idea can be extended to three dimensions. The term “topological insulator” (TI) was coined by one of the three groups, namely Moore and Balent [22], to describe this electronic state in 3D. The three groups showed there are four $Z_2$ invariants to fully characterize the topology of a material [22, 23, 24]. For simplicity, let’s consider a cubic system with lattice constant $a = 1$. The 3D Brillouin zone contains eight TRIM, as shown in Fig. 1.6. All the six surfaces of the Brillouin
zone possessed symmetries of the 2D Brillouin zone, so each of them has a $Z_2$ invariant. It has been shown that there are two constraints among them, which means only four of them can be independently determined. They are usually denoted as $(\nu_0; \nu_1, \nu_2, \nu_3)$, where $(\nu_1, \nu_2, \nu_3)$ are interpreted as Miller indices to specify the direction of layers.

A system is classified as a strong TI if $\nu_0 = 1$ and a weak TI if $\nu_0 = 0$ but $\nu_i = 1$ for some $i = 1, 2, 3$ [23]. Fu and Kane further shows that when a system is inversion symmetry invariant, the evaluation of $Z_2$ invariants can be greatly simplified. The values of each $Z_2$ can be conveniently determined by the parities of occupied Bloch wave functions at the TRIM [25].

A simple model of weak 3D TI ($\nu_0 = 0$) is stacking of layered 2D QSHIs. The left panel of Fig. 1.7 shows a possible Fermi surface for weakly coupled layers stacked
along $y$ axis. In this case the surface band intersects $E_F$ between $\Gamma_1$ and $\Gamma_2$ and between $\Gamma_3$ and $\Gamma_4$, which make the topology nontrivial. Here the topology does not protected these surface states because they can be localized by disorders.
Figure 1.6: Schematic of the Brillouin zone of a 3D cubic lattice including eight TRIM and six surfaces.

Figure 1.7: Fermi surfaces of TIs in the surface Brillouin zone. Left panel: weak TI; middle panel: strong TI, the surface state is helical in the sense that it is spin-polarized due to the spin-momentum locking; right panel: Dirac cone, the linear energy-momentum dispersion of surface states of strong TIs. Adapted from Ref. [5].
1.3.1 Strong topological insulators

Based on the bulk-surface correspondence, the odd number of gapless surface state is expected on the surface of an strong topological insulator. The effective Hamiltonian of the surface state is described as

\[ H_s = \hbar v \mathbf{k} \times \mathbf{\sigma} \cdot \mathbf{\hat{z}} = \hbar v (k_x \sigma_y - k_y \sigma_x) \]  

(1.17)

where \( \sigma_i \) are the Pauli matrices, and \( v \) is the Dirac velocity indicating a linear energy-momentum dispersion. Similar to the counter propagating edge channels with opposite spins in QSHIs, the surface state at momenta \( k \) and \( -k \) must have opposite spins due to the presence of TRS. In this sense, the surface state has a helical spin texture, which is illustrated in the middle and right panel of Fig. 1.7.

\( \text{Bi}_{1-x}\text{Sb}_x \) was the first 3D TI to be identified in the ARPES experiment performed by Hsieh et al. at Princeton [26], following the prediction by Fu and Kane [25]. This material is an alloy of Bi and Sb and owns two features: (1) band inversion at an odd number of TRIM and (2) opening of a band gap when the concentration of Sb is in a specific range. The 3D \( Z_2 \) invariants of \( \text{Bi}_{1-x}\text{Sb}_x \) are \((1;111)\) indicating it is a strong TI.

![Figure 1.8: Topological surface states of Bi\(_{1-x}\)Sb\(_x\): (a) ARPES results on the (111) surface of Bi\(_{1-x}\)Sb\(_x\). Along the direction from \( \bar{\Gamma} \) to \( \bar{M} \), The surface states cross \( E_F \) five times, which confirms its strong topological nature. (b) Schematic 3D Brillouin zone and the surface Brillouin zone of (111) surface. (c) The resistivity of Bi\(_{1-x}\)Sb\(_x\) as a function of temperature with different Sb concentrations. Adapted from Ref. [26].](image)

Experiments by Hsieh et al. directly identified both the bulk and surface band
structures of Bi$_{0.9}$Sb$_{0.1}$ using angle-resolved photoemission spectroscopy (ARPES). Fig. 1.8 provides a comprehensive mapping of gapless surface states as a function of momentum along the direction between $\bar{\Gamma}$ and $\bar{M}$ (projection of $L$ point at surface). The energy band structure of $L$ is observed, which is 3D massive Dirac-like dispersion. According to the theory, the Kramer’s degeneracy must be satisfied at TRIM $\bar{\Gamma}$ and three $\bar{M}$. And such degeneracy is indeed located at $\bar{M}$. Besides, as expected for a 3D TI, the Fermi energy crosses the surface bands five times between $\bar{\Gamma}$ and $\bar{M}$. This odd number shows that the material is a strong TI with $\nu_0 = 1$ and that these surface states are topologically protected from being backscattered by nonmagnetic disorders.

Another feature of 3D TI the coupling between spin and momentum, which was first observed in the subsequent experiments [27]. The surface states are non-degenerate away from TRIM and strongly polarized, providing even more strong evidence that this system is topologically nontrivial.

Figure 1.9: Crystal structure of the Bi$_2$Se$_3$ family. (a) 3D illustration of Bi$_2$Se$_3$ structure with three QLs. (b) The top view of A-B-C-A-B stack pattern. (c) side view of the stacking order of Bi$_2$Se$_3$. Adapted from Ref. [28].
The complicated surface band structure hinders potential realization of topologically based exotic properties. New 3D TI materials with more simple surface band structure became interest of study. In 2009, Zhang et al. [28] predicted that Bi$_2$Te$_3$, Bi$_2$Se$_3$ and Sb$_2$Te$_3$ are a class of 3D TIs which were shortly confirmed experimentally. A single Dirac-cone surface state for Bi$_2$Se$_3$ was observed independently by Xia et al. [29] and for Bi$_2$Te$_3$ by Hsieh et al. [30] and Chen et al. [31]. Sb$_2$Te$_3$ was measured together with Bi$_2$Te$_3$ by Hsieh et al. but the surface state was not confirmed because of the heavily p-type nature of the measured samples. The topological nature of Sb$_2$Te$_3$ was confirmed in thin-film samples afterwards [32].

Bi$_2$Te$_3$, Bi$_2$Se$_3$ and Sb$_2$Te$_3$ share the same rhombohedral structure with five layers of atoms in one unit cell. Fig. 1.9(a) shows the structure of Bi$_2$Se$_3$, which has layer structure. It consists of five-atom layer along z-axis known as quintuple layers (QLs). Each QL consists of five atoms stacked in A-B-C-A-B-··· manner and with two equivalent Se atoms, two equivalent Bi atoms and a third Se atoms, as shown in Fig. 1.9(b). The binding is strong within a QL due to covalence bonding but much weaker between neighbor QLs with van der Waals interaction.

Figure 1.10: Energy-momentum dependence of the LDOS for (a) Sb$_2$Se$_3$, (b) Sb$_2$Te$_3$, (c) Bi$_2$Se$_3$, (d) Bi$_2$Te$_3$ on the (111) surface. The surface states are located around $\bar{\Gamma}$ point in the band gap of bulk states in Sb$_2$Te$_3$, Bi$_2$Se$_3$ and Bi$_2$Te$_3$. No surface state exists in Sb$_2$Se$_3$. Adapted from Ref. [28].
This family of TIs is appealing because of their simple surface band structures compared with that of Bi\(_{1-x}\)Sb\(_x\). The 3D \(Z_2\) invariants are (1;000), and there is only one Dirac cone of surface state located at \(\Gamma\) point of surface Brillouin zone. The calculated surface state dispersion in the band gap of this family is shown in Fig.1.10 adapted from Ref. [28]. The theoretical result indeed confirms the single Dirac point at \(\Gamma\) in Bi\(_2\)Te\(_3\), Bi\(_2\)Se\(_3\) and Sb\(_2\)Te\(_3\), while there is not surface states in Sb\(_2\)Se\(_3\). The simplicity greatly eases the experimental investigation of the properties of surface state. From the technical point of view, the stoichiometric composition makes high-quality synthesis relatively simple.

![Figure 1.11: ARPES measurements of surface band dispersion on Bi\(_2\)Se\(_3\) (111) surface.](image)

(a-c) Single Dirac cone of surface states close to \(\bar{\Gamma}\) point along the \(\bar{\Gamma}-\bar{M}\) and \(\bar{\Gamma}-\bar{K}\) directions. (d) Schematic of helical spin texture of the Dirac cone. Adapted from Ref. [29].

Xia et al. observed the single Dirac cone of surface states in Bi\(_2\)Se\(_3\) [29], as shown in Figs. 1.11(a-c). Its bulk band gap is around 0.3 eV. This indicates that the topological properties of the material with high purity can be studied at room temperature. The Fermi energy inside the band gap is located rather close to the conduction band minimum. Also, the surface state is an ideal Dirac cone with only slight curvature and spin polarized as well, which is shown schematically in Fig. 1.11(d).

In contrast, the band structure of Bi\(_2\)Te\(_3\) is more complicated [33]. Fig. 1.12(a) indicates that the Dirac point is located beneath the valence band maximum, which
Figure 1.12: ARPES measurements of constant-energy contours of the surface states. The intensity of surface states from low to high corresponds to the colors from blue to red. Arrows point to the position of maximum in LDOS. The surface state presents hexagonal warping. Adapted from Ref. [33].

makes it difficult to measure the transport property of surface state. Another difference between Bi$_2$Te$_3$ and Bi$_2$Se$_3$ is the energy contour of Bi$_2$Se$_3$ is almost circular, while it presents hexagonal warping in Bi$_2$Te$_3$, as shown in Figs. 1.12(b-e). Interestingly, the warping can be utilized to explore the dispersion of surface states such as quasiparticle interference.

For Sb$_2$Te$_3$, the detailed band structure was explored by Jiang et al. in 2012 through the scanning tunneling spectroscopic measurement [34]. As demonstrated in Fig. 1.13(c), the $dI/dV$ spectrum under zero magnetic field shows the sharp increase in the local density of states(LDOS) at around 0 and 300 meV, indicating that the bulk energy gap is $\sim$ 300 meV which agrees with the calculation. In the bulk gap, a V-shaped spectrum with a minimum conductance representing Dirac point at 100 meV above $E_F$ is observed, which is just the topologically protected surface state.
Figure 1.13: (a-b) Topographic images taken on the surface of $\text{Sb}_2\text{Te}_3$. Point defects can be visualized in (b). (c) Bulk and surface spectra inside the band gap. The linear dependence confirms the existence of the Dirac cone. (d) Landau quantization of topological surface states. Adapted from Ref. [34].

1.4 Topological materials beyond topological insulator

With the theoretical development and experimental realization of topological insulating state, people also discovered a variety of novel states associated with the TI. More intriguing exotic properities may be realized if an energy gap of surface states of TI is induced by breaking the TRS [5]. If the TRS is broken by external magnetic field or proximity to a magnetic material, an axion insulator may be achieved, which possesses topological magnetoelectric effect. If the ferromagnetism (FM) can be established in the TI material, the quantum anomalous Hall (QAH) state may
be achieved. On the other hand, if one combine topological insulator with a superconductor, the correlated interface is predicted to host Majorana fermion excitations, which refers to a fermion that is its own antiparticle [35]. It has been proposed to be the basis of a fault-tolerant quantum computer and memory [36].

Theorists also propose that across the topological phase transition, novel topological phases such as topological semimetal emerge. Topological semimetals, including Weyl semimetal, Dirac semimetal and nodal-line semimetal, are different from ordinary semimetals in the sense that they have non-trivial topology [37]. In this section, I will selectively introduce QAH insulator and topological Weyl semimetal, which are directly related to the works presented in the thesis.

1.4.1 Quantum anomalous Hall insulator

The quantum anomalous Hall effect (QAHE) can be viewed as the quantized version of the anomalous Hall effect (AHE). The AHE refers to the non-zero Hall conductivity in the absence of the external magnetic field. There are several competing mechanisms of the AHE, such as disorders, the Berry phase [38]. With the discovery of quantum Hall effect, it is natural to search for a similar quantized version of AHE. Although the first explicit model of QAHE is the Haldane model proposed in 1980 as mentioned above, it was not experimentally realized until the topological classification of insulating states was established. The QSHI is regarded as a ideal platform to realize the QAHE, as it consists of two copies of chiral edge modes with opposite propagating directions and opposite spin polarizations, which are protected by the TRS. As long as one of the edge channels is lifted by breaking the TRS, the Hall conductance will become quantized. Following this idea, it was predicted that the QAHE can be realized by doping Mn into the HgTe/CdTe quantum well structure. However, the magnetic coupling of Mn spins are paramagnetic instead of ferromagnetic, so a small external magnetic field is necessary to induce the QAH phase, which hinders the confirmation of the true QAHE [39].
Similary to QSHI, 3D TIs are also deeply related to the QAHE. The realization of QAHE is also proposed in magnetically doped 3D TIs in the family of Bi$_2$Se$_3$ [40]. As an intrinsic perpendicular magnetization is established, the TRS of a 3D TI film can be broken. Consequently, the 2D gapped surface bands of top and bottom surfaces have distinct topological characters. Each surface has half-quantized Hall conductance $\sigma_{xy} = e^2/2h$. The Hall conductance of two surfaces adds up to a full quantized Hall conductance, as illustrated in Figs. 1.13. By tuning $E_F$ of the sample into the magnetically induced gap of surface bands, one should be able to observe a Hall conductance plateau $\sigma_{xy} = e^2/h$ and a vanishing longitudinal conductance $\sigma_{xx} = 0$. Experimental realization of this idea was first achieved in chromium(Cr)- and vanadium(V)-doped (Bi,Sb)$_2$Te$_3$. The QAHE emerges when the bulk carrier density is tuned to a value close to zero by applying a gate voltage. The Hall conductance is quantized to $\pm e^2/h$ at zero magnetic field, which agrees with the anomalous nature of the QAHE [41, 42]. More recently, Ou et al. achieved a significant increase of the characteristic QAH temperature in Cr/V co-doped (Bi,Sb)$_2$Te$_3$ films [43], where the critical temperature enhancement has been attributed to the improvement of the FM order [41, 42, 44, 45, 46].

![Figure 1.14: Schematic of quantized Hall conductance of magnetically doped 3D TI. The top and bottom surface each contributes half of a quantized Hall conductance.](image-url)
1.4.2 Topological Weyl semimetal

As introduced above, the surface state in TIs is protected by the TRS and robust against weak disorders and gives exotic properties. Interestingly, similar to the TIs, the topological surface states also exist on the surface of a class of topological semimetals called topological Weyl semimetal (TWS). Because of the non-trivial topology, TWS further expands the collection of topological materials [47, 48].

In 1929, Weyl first found a massless Dirac fermion in the Dirac equation with non-zero chirality [49], which is later call Weyl fermion. In this sense, the massless Dirac fermions are considered as a pair of degenerate Weyl fermions whose chiralities cancel out. The Hamiltonian of a Weyl fermion is described as

$$H(k) = \pm v_F \sigma \cdot k,$$

where the sign represents its chirality. Among all the elementary particles, neutrino was once a possible candidate of Weyl fermion. However, neutrinos were later found to be massive. An example of a Weyl fermion has been unknown until recently it was theoretically proposed to emerge in condensed matter systems [50, 51, 52, 37]. A solid-state material hosting Weyl fermions is called a TWS, where the low-energy electron excitations behave like Weyl fermions due to the non-trivial topology of their band structures. The Weyl node refers to the crossing point of the valence band and conduction band in the Brillouin zone, where the bands disperse linearly in 3D momentum space. Similar to the TIs, the emergence of Weyl points also originates from the band inversion induced by the SOC, as illustrated in Fig. 1.15. The topology can be characterized by the Berry curvature near the Weyl points. The eigenstate of the Hamiltonian in Eq. 1.18 can be solved, from which the Berry curvature can be computed based on Eq. 1.7:

$$\Omega(k) = \pm \frac{k}{2k^3}.$$  

As discussed in Chapter 1.1, the Berry curvature is equivalent to a “magnetic field” in momentum space. Apparently, the Berry curvature becomes singularity at
the Wely node, which means the Weyl node is a “magnetic monople” with fixed chirality, being either a source or a sink of the Berry curvature. The Chern number associated with a 2D Fermi surface (FS) enclosing a Weyl node is then calculated:

\[ C = \frac{\gamma [FS]}{2\pi} = \frac{1}{2\pi} \int \Omega(k) \cdot \mathbf{S} = \pm 1. \tag{1.20} \]

Therefore, the Weyl points with opposite chirality are also regarded as opposite topological charges. In solid-state crystals, the net chirality of the bulk must be zero, so the Weyl fermions in these materials always emerge in pairs with opposite chiralities. Consequently, they can only be created or annihilated in pairs, being otherwise stable to weak translation-preserving perturbations [53, 54]. From the symmetry point of view, if the TRS and inversion symmetry coexist, the Berry curvature must be zero everywhere. In order to lift the chirality degeneracy, either TRS or inversion symmetry needs to be broken. Thus Weyl nodes generically occur in 3D magnetic or noncentrosymmetric materials with the strong SOC. What makes TWS appealing is the exotic electronic properties, such as the open surface Fermi arc [50, 55] and the chiral anomaly in transport measurements [56, 57, 58, 59, 60, 61, 62].

**Fermi arcs**

If the Weyl nodes locate at \( E_F \), the Fermi surface exhibits an unclosed line that connects the projections of a pair of Weyl nodes with opposite chirality on the corresponding surface, namely the Fermi arc within the BZ. Such surface state is clearly different from that of TI, normal insulator or normal metal. The open arc can be illustrated by the following construction. Consider a simple rectangular bulk BZ and the surface BZ of \( xy \) surface as our interest, where there are two Weyl nodes separated in \( k_y \) direction, as shown in Figs. 1.15(a-b). We apply the cylindrical coordinate frame \((k_0, \theta, k_z)\), where \( k_0 = \sqrt{k_x^2 + k_y^2} \) and \( \theta = \tan^{-1}(k_y/k_x) \). If \( k_0 \) is fixed, then the Hamiltonian is reduced to a 2D gapped Hamiltonian \( H(\theta, k_z) \), with \( \theta \) and \( k_z \) as the two momenta. The two momenta \( \theta, k_z \) define the surface of a torus in the momentum space. The Chern number of this 2D Hamiltonian is then given by
Eq. 1.20,

\[ C = \begin{cases} 
1 & \text{enclosing } W_+ \\
-1 & \text{enclosing } W_- \\
0 & \text{otherwise.} 
\end{cases} \] (1.21)

Figure 1.15: Surface Fermi arc in TWS. (a) The 3D BZ of a TWS with two Weyl nodes separated in \( k_y \) direction. (b) The surface BZ of \( z = 0 \) surface. (c) The cylinder unrolled onto a plane gives the spectrum of the two-dimensional subsystem \( H(\theta, k_z) \) with a boundary. On top of the bulk spectrum, a chiral state appears due to the nonzero Chern number.

Consider a 2D surface of \((\theta, k_z)\) illustrated in Fig. 1.15(a). As the Weyl points \( W_+ \) is enclosed, we expect a chiral edge state at the boundary of \( z = 0 \) (Fig. 1.15(c)). The edge state (or surface state in 3D) crosses \( E_F \) at a certain value of \( \theta \), which corresponds to an individual \( k \) point in the surface Brillouin zone, as illustrated in Fig. 1.15(c). Now by slowly varying the value of \( k_0 \), the space enclosed in the 2D torus of \((\theta, k_z)\) changes accordingly. Fig. 1.16 demonstrates this process. As long as there is only one Weyl node in it, the surface state is guaranteed. Note that once the other Weyl node is also enclosed, the Chern number becomes zero and no odd edge states exist any more. Thus the surface state is a unclosed arc that mush begin at
one Weyl point and end at the other Weyl point with opposite chirality. The unique Fermi arc serves as a strong evidence for identifying a TWS using surface-sensitive techniques.

Figure 1.16: Illustration of surface states arising from bulk Weyl points. When varying the $k_0$, the 2D torus expands, the Fermi surface is a continuous surface state in a shape of arc, beginning at one Weyl Node and ending at the other.

**Topological Weyl materials**

The observable properties of TWS will exist only when the Weyl nodes are located close to $E_F$ and there are no other states in the band that may hinder the effects induced by the Weyl nature. The locations of Weyl nodes relative to $E_F$ is not guaranteed by anything, so it is not a trivial task to find a real topological Weyl material. The first type of Weyl fermion was predicted and observed in TaAs family of compounds in 2015 [63, 64, 65, 66]. It is formed by a linear crossing of the valence band and conduction band in the BZ. The Fermi surface of the bulk stats in type-I TWS shrinks to zero at the Weyl nodes when the Weyl nodes are sufficiently close to $E_F$. Interestingly, in the surface spectrum, this results in the appearance of open Fermi arcs, connecting the projections of opposite chirality Weyl points to the surface.
Shortly after the type-I Weyl fermions were demonstrated, Ref. [67] proposed type-II TWSs, in which the linear dispersion is tilted so that Weyl points appear at the touching points of electron and hole pockets, as shown in Fig. 1.17. Unlike type-I Weyl points, these Weyl points always have an open Fermi surface (when the Hamiltonian is linear in momentum), resulting in the unusual chiral anomaly [68]. Type-II Weyl fermion was predicted in several transition metal dichalcogenides (TMD): WTe$_2$ [67], MoTe$_2$ [69, 70] and Mo$_x$W$_{1-x}$Te$_2$ [71].

Figure 1.17: Two types of TWS: (a) The type-I TWS. The Fermi surface shrinks to zero at the Weyl nodes given that $E_F$ is very close to the Weyl nodes. (b) The type-II TWS. The Dirac cone near the Weyl node is tilted. The Fermi surface consists of electron and hole pockets

1.5 Impact of Point defects on solid state materials

Point defects and impurities play a significant role on determining the electronic, magnetic or chemical properties of solid materials and have a decisive impact on their performance in practical applications [72]. A well-known example is the role of defects in semiconductor technology, the foundation of numerous modern electrical devices. Point defects in semiconductors often give rise to shallow donor or acceptor centers, making the material highly conductive. By carefully controlling the concentration of these shallow donor and acceptor impurities, a wide range and high precision of conductivity can be achieved. What makes semiconductor really useful is that the concentrations of shallow donors and acceptors can be made spatially inhomogeneous
in a controllable way. The incorporation of inhomogeneous impurity distribution in semiconductors can be exploited to fabricate complicated electronic devices like diodes, transistors or complex integrated circuits. None of modern electronic devices would be possible if impurities were not judiciously introduced in semiconductors [73, 74].

Impurities also have a significant impact on strongly correlated materials in condensed-matter physics. A notable example is superconductivity. In conventional superconductors such as Nb or Pb, the magnetic impurity atoms suppress the critical temperature by breaking the Cooper pairs via spin-flip scattering [75]. In unconventional high-$T_c$ superconductors, in contrast, both magnetic and non-magnetic impurities cause dramatic effects [76]. Hole doping in the form of excess oxygen dopants drives the cuprates from antiferromagnetic phase into high-$T_c$ superconducting phase [77]. In addition, dopant inhomogeneity results in the observable electronic inhomogeneity in the high-$T_c$ superconductors on the nanoscale [78, 79].

Since the birth of TI, the doping effect of various non-magnetic and magnetic impurities is very important for the performance of TIs. They can affect the carrier concentration, magnetoresistance and thermoelectric properties of materials [80]. For example, the superconductivity can be induced in TI by properly doping with non-magnetic impurities. It has been experimentally demonstrated that $\text{Cu}_x\text{Bi}_2\text{Se}_3$ ($x = 0.12 \sim 0.15$) is superconducting at $T_c = 3.8$ K [81, 82, 83]. More doped TIs were found superconducting after that [84, 85]. The carrier concentration in TI can be tuned by dopants. In 2011, Hor et al. demonstrated that $E_F$ of Ca-doped $\text{Bi}_2\text{Se}_3$ single crystals can be moved into the band gap, so the carrier type was tuned from n-type to p-type [81]. Magnetic impurities break the TRS. If the FM order can be established, a band gap of surface states opens, which may induce exotic properties, such as the QAHE. The experimental realization of the QAHE has been addressed in the prior section.

Beside the artificial doping, native defects in most TI materials exist inevitably.
Many known TIs are doped semiconductors with dominant bulk conduction due to native defects, which hinders the realization of interesting phenomena. For example, nominal Bi$_2$Se$_3$ single crystals are n-type doped, while nominal Sb$_2$Te$_3$ single crystals are p-type doped. One of the major hurdles in TI research is the lack of clear identification and understanding of the widely-existing native defects, which is crucial for optimization of synthesis and device fabrications. Local probe techniques such as scanning tunneling microscopy, are particularly useful to address this issue.

1.6 Scope of this thesis

Chapter 2 introduces basic concepts of scanning tunneling microscopy/ spectroscopy (STM/STS) and the practical procedures to conduct STM measurement. Chapter 3 is dedicated to the study of the impact of native defects on 3D TI Bi$_2$Se$_3$ and our experimental efforts on tuning $E_F$ by doping calcium in Bi$_2$Se$_3$ thin films. Chapter 4 is about the topological phase transition in (Bi$_{1-x}$In$_x$)$_2$Se$_3$ single crystals, across which we visualized a microscopic inhomogeneity of nano-topological region and nano-normal region. Chapter 5 presents the defect states of magnetic defects Cr and V in 3D TI (Bi,Sb)$_2$Te$_3$. We observed very unique spatial distributions of local density states of magnetic defects, which will serve as an electronic fingerprint to study QAH materials. Chapter 6 is about the quasiparticle interference of surface states of type-II topological Weyl semimetal WTe$_2$. Our results provide solid evidence of existence of surface Fermi arcs in WTe$_2$. In Chapter 7, I will conclude the thesis.
Chapter 2
Scanning Tunneling Microscopy and Spectroscopy

Scanning tunneling microscopy (STM) is one of the most powerful techniques to study the electronic properties with atomic resolution in real-space. In 1981, Gerd Binnig and Heinrich Rohrer invented and implemented the first working STM in IBM zurich, and won the Nobel prize in physics in 1986 for their invention. STM works based on the concept of quantum tunneling and can be viewed as a combination of three parts: scanning, electron tunneling and point probing, which make STM a unique microscopy tool [86, 87]. First, Unlike other types of electron microscopes, STM does not use optical lens, so there is no image distortion caused by optical aberration. The electron tunneling occurs in the energy range typically within 1 eV, in contrast to other high-energy electron microscopes using electron beams with the energies of keV to MeV, so it is easier to achieve high energy resolution (i.e., meV-µeV). Besides, the electron energy is smaller than typical chemical bonding energy, so STM allows non-destructive imaging without radiation-induced damages.

The most important feature of STM is the local information it provides with atomic resolution in real-space. Therefore, STM is complimentary to the diffraction techniques, which probe spatially average properties such as crystal structures in condensed matter. The local information is particularly useful for studies of non-periodic features such as defects, disorders and electronic or chemical inhomogeneity in solids [88, 89, 90, 91]. Since its birth, STM has been proven successful in the investigation of these non-periodic features in complex materials such as semiconductors, superconductors and low-dimensional quantum materials [92, 93, 94, 95]. Therefore, STM is an powerful microscopic method to study the impact of point defects on the topological
properties in quantum materials. In this chapter, I will introduce the basic principles of quantum tunneling and briefly explain the basic experimental procedures involved in this work.

2.1 Theory of Quantum tunneling phenomenon

2.1.1 An elementary model of tunneling

STM/STS are based on quantum tunneling phenomena. The quantum tunneling effect describes a quantum process allowing electrons penetrating through a classically forbidden energy barrier where the potential of barrier is higher than the energy of electrons.

Figure 2.1: The difference of classical regime and quantum regime. In the quantum regime, electrons have non-zero probability of tunneling through the classically-forbidden energy barrier.

Quantum tunneling can be illustrated in a simplified one-dimensional model. In the classic regime, a free electron with energy $E$ and potential $U(z)$ is described by

$$\frac{p_z^2}{2m} + U(z) = E,$$  \hspace{1cm} (2.1)
where $m$ is the electron mass and $p_z$ is the electron momentum. In the situation of $E > U(z)$, the electron has non-zero $p_z$, while the electron cannot penetrate the potential barrier where $E < U(z)$. In the quantum mechanics regime, the state of electron is described by wave function $\psi(z)$ which satisfies the Schrödinger’s equation
\[-\frac{\hbar^2}{2m} \nabla^2 \psi(z) + U(z)\psi(z) = E\psi(z). \tag{2.2}\]

Consider the step-function-like potential shown in Fig. 2.1. The solutions of Eq. 2.2 in classically allowed and forbidden regions are
\[\psi(z) = \psi(0)e^{\pm ikz} \tag{2.3}\]
\[\psi(z) = \psi(0)e^{\pm \kappa z} \tag{2.4}\]

where the wave vector is $k = \sqrt{2m(E-U)/\hbar}$ in the classically allowed region and the decay constant is $\kappa = \sqrt{2m(U-E)/\hbar}$ in the classically forbidden region. One of the solutions of Eq. 2.4 with the plus sign is physically unreasonable, because the wavefunction won’t exponentially increase. Thus the probability of observing an electron in the potential barrier is then described as $|\psi(0)|^2e^{-2\kappa z}$, which is non-zero but exponentially decays inside the barrier.

By generalizing this elementary model to metal-insulator-metal junction, we are able to explain some basic features of tunneling between tip and samples in STM, which is shown in Fig. 2.2. When the tip is brought very close to the sample (typically 3–10 Å) but without physically touching, the overlapped wave functions of two electrodes are linked by an exponentially decaying term
\[|\psi_{\text{tip}}|^2 \sim |\psi_{\text{sample}}|^2 e^{-2\kappa W}, \tag{2.5}\]

where $W$ is the thickness of the tunneling junction and the decay constant of wave functions $\kappa = \sqrt{2m\phi/\hbar} \sim 0.51\sqrt{\phi(\text{eV})}\text{Å}^{-1}$. The apparent energy barrier $\phi$ describes the minimum energy an electron takes to escape from metal surface to the vacuum. Here $\phi$ equals the work function and depends on materials, but the values of common
metals fall into the range of $4 - 6 \text{ eV}$. With this, it is reasonable to estimate $\kappa \sim 1 \text{ Å}^{-1}$ given $\phi = 4 \text{ eV}$. Consequently, the tunneling probability decreases $e^2 = 7.4$ times as the tip-sample distance increases by 1 Å. This exponential dependence results in an extremely high sensitivity of tip-sample separation.

When $E_F$ of the tip and the sample aligns with each other, an electron can hop from the tip to the sample or vice versa, but there is no net tunneling current. As a bias voltage $V$ is applied between them, $E_F$ of the sample is lifted with respect to that of the tip. The tunneling current is then proportional to the number of states on the sample in the energy range $(E_F - eV, E_F)$. By considering all the states within this range, the tunneling current is

$$I \propto \int_{E_F - eV}^{E_F} |\psi_s(0)|^2 e^{-2\kappa W} d\epsilon. \tag{2.6}$$

Because of the logarithmic dependence of $\phi$ on the tunneling current $I$, $\phi$ can be conveniently measured by varying the tip-sample distance with an AC voltage,

$$\phi \approx 0.95 \left(\frac{d \ln I}{dW}\right)^2. \tag{2.7}$$
In this elementary one-dimensional model discussed above, the exponential dependence of the tunneling current on the thickness of energy barrier is established. STM experiments are usually conducted with a very short tip-sample distance. It is shown that the typical tip-sample distance is $3 - 7 \text{ Å}$, which is on the microscope scale. In this distance range, the overlap of tip potential and sample potential in the gap becomes important, which will substantially lower the energy barrier of tunneling electrons in the junction as shown in Fig. 2.3. However, it has been that the apparent barrier height $\phi$ is almost constant down to several angstrom. In realistic case, prior experiments show that the measured apparent barrier height persists constant down to almost a mechanical contact [87]. It indicates that the exponential decaying dependency of the tunneling current on the tip-sample distance is valid in the normal tunneling range. In the next part, an more rigorous derivation of the transmission probability based on the Bardeen approach will be introduced.

![Graph](image)

Figure 2.3: The calculated apparent barrier height and actual potential barrier as a function of barrier thickness. The actual barrier drops significantly due to the existence of image forces. However, the apparent barrier height persists a value close to a constant in the normal range of $W$. 
2.1.2 The Bardeen approach to tunneling theory

The most widely used theoretical model for STS is proposed by Bardeen in 1960 based on perturbation theory [96], as shown in Fig. 2.4. It satisfactorily interpreted the experimental demonstration of metal-insulator-metal tunneling junctions by Giaever [97], which was a critical evidence for the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity [98].

Bardeen first treated the electronic states of tip and sample as two separate subsystems by solving the corresponding static Schrodinger’s equations. The tunneling probability of electrons in between is then described by tunneling matrix shown in the following equation

\[
M = \frac{\hbar}{2m} \int \Sigma (\chi^* \frac{\partial \psi}{\partial z} - \psi \frac{\partial \chi^*}{\partial z})dS, \quad (2.8)
\]

where \( \chi \) and \( \psi \) are the wave functions of electrons on the tip and the sample, respectively. Based on the Fermi golden rule, the transfer rate is

\[
w = \frac{2\pi}{\hbar} |M|^2 \delta(E_\Psi - E_\chi). \quad (2.9)
\]

The \( \delta \) function indicates an elastic process, in which the energy of tunneling electrons must be conserved. The total tunneling current is consequently solved by integrating the tunneling probability \( w \):

\[
I = \frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} \left[ f(E_F - eV + \epsilon) - f(E_F + \epsilon) \right] \rho_s(E_F - eV + \epsilon) \rho_t(E_F + \epsilon) |M|^2 d\epsilon, \quad (2.10)
\]

where the Fermi distribution function is \( f(E) = \{1 + e^{(E-E_F)/k_B T}\}^{-1} \), and \( \rho_s(\epsilon) \) and \( \rho_t(\epsilon) \) are the density of states(DOS) of sample and tip. \( E_F \) in Eq. 2.10 specifically represents the Fermi level of the tip, and thus the Fermi level of the sample is \( E_F - eV \).

Since the experiments discussed in this work were mainly conducted at a base temperature of \( \sim 5 \) K, the thermal excitation of electrons \( k_B T \sim 4 \) meV is much smaller than the energy resolution of interest, and hence \( f(E) \) can be simplified as a step function whose value is 1 as \( E < E_F \) and 0 as \( E > E_F \). In addition, based on
Figure 2.4: Schematic of Bardeen approach of tunneling spectroscopy. Bardeen used perturbation theory in his theory and treated the tip and sample as two uncoupled systems. The tunneling current is calculated through the overlap of two subsystems using Fermi golden rule.

the experiment conducted by Geiver [97], Bardeen further assumed that the matrix element is energy independent. With these conditions, the tunneling current is then reduced to a convolution of DOS of two electrodes,

\[ I \propto e^{-2\kappa z} \int_{-\infty}^{\infty} \rho_s(E_F - eV + \epsilon)\rho_T(E_F + \epsilon)d\epsilon. \]  

(2.11)

In realistic experiments, the DOS of sample \( \rho_s(E) \) is really of our interest. If the tip can be carefully prepared and characterized so that \( \rho_t(E) \) does not vary appreciably in the required energy interval, we can further derived that

\[ \frac{dI}{dV}(V) \propto e^{-2\kappa z}\rho_s(E_F - eV). \]  

(2.12)

2.2 Experimental realization and measurement modes

The operation of STM is based on the tunneling effect explained in the prior section between an atomically sharp tip and a conductive sample. The core part of
STM typically consists of four basic units: a conductive tip as probe, an piezoelectric tube to move the tip, a current amplifier and an electric control unit. As depicted by the schematic in Fig. 2.4, a DC bias voltage is applied in the operation of STM between the probe tip and the sample when the tip is brought very close to the sample surface by a coarse motor. The tunneling current (~1 pA–1 nA) caused by the bias voltage is then amplified by a current amplifier with gain of 0.1–10 GΩ, which converts the tiny current to a large voltage signal.

Figure 2.5: Schematic diagram of core parts of scanning tunneling microscope. A DC bias voltage is applied between the probe tip and the sample when the tip is brought very close to the sample surface. The tunneling current (~1 pA–1 nA) caused by the bias voltage is then amplified by a current amplifier with gain of 0.1–10 GΩ, which converts the tiny current to a large voltage signal. Figure source: Michael Schmid, TU Wien

2.2.1 Constant current topographic imaging

Due to the ultrahigh $z$ sensitivity, one of the most common modes conducted by STM is the constant current mode. In order to persist a constant tunneling current
between the two electrodes, the amplified signal is immediately compared with a preset reference value ($I_{set}$) in the electric control unit which drives the $z$-piezo with negative feedback. The feedback loop controls the $z$-piezo to extend or withdraw to ensure the current is fixed. With the feedback loop on, scanning voltages can be applied on the $xy$-piezo to move the tip laterally line by line over the sample surface, during which the height of the tip will be recorded with lateral coordinates. One would end up with an 2D contour of height profiles of the surface under the constant tunneling current, namely STM topographic imaging. The topographic imaging is particularly a efficient and powerful mode to image the sample surface with atomic resolution.

Under the constant current mode, the tunneling is only sensitive to the bias voltage. The negative feedback system persists a constant current, 

$$I(x) = I_0 e^{-\kappa z} \int_0^{eV} \rho_s(x, \epsilon) d\epsilon = \text{constant.}$$

(2.13)

where $x \equiv (x, y)$ is the lateral coordinate. The height profile measured by STM can be derived as 

$$z(x) = -\kappa^{-1} \ln\left(\frac{I}{I_0}\right) + \kappa^{-1} \ln\left(\int_0^{eV} \rho_S(x, \epsilon) d\epsilon\right).$$

(2.14)

The current contour in the topographic images contains information from both the atomic contour of sample surface as well as the integral of LDOS of the sample between $E_F$ and $E_F + eV$.

In practice, when the sample bias is large, e.g. $\pm 1$ V, the integrated local density of states(LDOS) usually varies little over the sample surface, in which condition a topographic image mainly reflects the atomic contours of sample surface, also known as the morphology. Fig. 2.6(a) shows a topographic image of the (111) surface of single crystal Au at $-1$ V. The image contrast indicates the existence of an atomic step edge and a couple of individual adatoms. On the other hand, as the absolute value of sample bias gets relatively small, e.g. $< 200$ mV, the effect of nonuniform integrated LDOS becomes measurable on the topographic image if the LDOS of sample varies
significantly. Fig. 2.6(b) shows another topographic image of Au(111) surface taken at $-0.2 \, \text{V}$, where quasiparticle interference patterns of surface states near the step edges and adatoms emerge.

Figure 2.6: Topographic images of atomically flat Au(111) surface. (a) is taken at $-1 \, \text{V}$. A step edge and several individual adatoms are observed on the surface. (b) is taken at $-0.2 \, \text{V}$ where Friedel oscillation patterns emerge near the imperfect structures. The patterns are due to the varied integrated LDOS over the surface. The scale bars represent 15 nm. The herringbone patterns on Au(111) is due to the surface reconstruction of $22 \times \sqrt{3}$ structure.

2.2.2 Spectroscopic imaging

As exemplified in the prior section, the effect of integrated LDOS can be observed in the topographic measurement at low sample bias. Yet the LDOS of the sample, which is proportional to the differential conductance as shown in Eq.2.12, can be thoroughly studied in another powerful operation mode, namely spectroscopy mode. In this mode, the feedback loop is temporarily deactivated and the sample bias sweeps from one value to another value, during which the tunneling current changes accordingly as a function of bias voltage. More importantly, during the process, an AC modulation voltage $V_{\text{mod}}$ with small amplitude of 0.1-20 mV and typical frequency of 0.5-2 kHz is added to the DC bias voltage. The amplitude of AC portion of current
Figure 2.7: $dI/dV$ spectrum taken on the surface of topological insulator Bi$_2$Se$_3$. V-shaped surface states are visualized near the Dirac point located at $E_F - 0.15$ eV. The band gap is $\sim 0.3$ eV. These features are consistent with the band structure calculation and measurement reported by other techniques.

in response to $V_{\text{mod}}$ at the same frequency is $\Delta I(V_0) = \frac{dI}{dV}(V_0) \cdot V_{\text{mod}}$. Thus the differential conductance satisfies $\frac{dI}{dV}(V) = \Delta I(V)/V_{\text{mod}}$. The small AC current signal $\Delta I(V)$ can be measured accurately by the lock-in amplifier, which uses a technique known as phase-sensitive detection. Eventually, The output value of lock-in amplifier is associated with the differential conductance by

$$V_{\text{lock-in}} = \frac{dI}{dV} \times V_{\text{mod}} \times R_{\text{gain}} \times \frac{V_{\text{scale}}}{Sens}, \quad (2.15)$$

where $V_{\text{mod}}$ is the rms of AC modulation, $R_{\text{gain}}$ is the gain of preamplifier, $Sens$ is the sensitivity of the lock-in amplifier and $V_{\text{scale}}$ is the scaling range of output signal of the lock-in amplifier. Fig. 2.7 shows an example of $dI/dV$ spectrum measured on the surface of Bi$_2$Se$_3$. One can observe the V-shaped topological surface states in the band gap and the Dirac point being $\sim 150$ meV below $E_F$.

With deliberately designed system with good vibration isolation and long continuous operating time, it is possible to conduct experiments with the spectroscopic imaging mode, in which the differential conductance measurement can be performed
on each single pixel of a grid. The feedback loop is activated to enable the tip to move between two adjacent pixel and deactivated while a single $dI/dV$ spectrum is taken. This mode is also known as “$dI/dV$ grid mapping” or simply “spectroscopy mapping”. In our STM system, a typical mapping consists of $100 \times 100$ pixels with 200 energy points in each spectrum, which takes approximately 30 hours.

2.3 Experimental procedures

The experiments discussed in this work were carried out with an Omicron low-temperature ultrahigh vacuum (UHV) STM. It consists of an STM chamber with STM scan-head for actual scanning measurement, a preparation chamber for sample surface treatment and other surface characterization methods, and a load-lock chamber for fast sample transferring.

2.3.1 Achievement and maintenance of ultrahigh vacuum

For the best performance of STM, an UHV ($\leq 5 \times 10^{-10}$ mbar) environment is required, because free gas molecules would cause contamination or oxidation on the sample surface or affect the stability of tunneling junction. To achieve such UHV environment from atmospheric pressure, the gas in the UHV chambers need to be pumped out by a combination of different types of pumps. An turbomolecular pump connected with a mechanical back pump (or roughing pump) is applied to pump the chamber down to the high vacuum range ($\sim 10^{-7}$ mbar). In this range, the parts and the chamber wall will outgas significantly as they absorb water, air molecules and hydrocarbons on their surfaces when they are exposed in the air.

True UHV conditions in the range of $10^{-9} - 10^{-11}$ mbar can only be achieved after the system is baked out properly for a sufficient amount of time, which can expedite the outgassing of chamber walls. To achieve this, the entire system is heated up to $150^\circ$C for around 60 hours, during which the turbomolecular pump is kept on.
After the bake-out process, the pressure will be able to decrease to $10^{-8}$ mbar range. An ion pump takes over and further evacuate the chamber down to $10^{-11}$ mbar range. And a titanium sublimation pump will also be run occasionally to help accelerate the pumping process. It normally takes approximate 5 to 7 days to achieve a pressure of $8 \times 10^{-11}$ mbar from atmospheric pressure. In our system, both the STM chamber and the preparation chamber are kept in the UHV conditions and the base pressure is $\lesssim 2 \times 10^{-11}$ mbar. The pressure is monitored by ionization gauges.

2.3.2 Cryostat for low-temperature measurements

The cryogenic system of our STM consists of two bath cryostats: The outer cryostat is always filled with liquid nitrogen (LN$_2$) to provide thermal isolation. The inner cryostat can be filled with either LN$_2$ or liquid helium (LHe) to achieve 77 K or 5 K respectively. With the current setup, the LN$_2$ in the outer cryostat lasts for 48 hours, and the inner cryostat can last up to 60 hours at 5 K and 14 days at 77 K.

The inner cryostat can also be pumped by a mechanical pump to a base temperature of $\sim 48$ K, as the nitrogen becomes solid due to the reduced pressure. In this condition, the cooling power comes from the sublimation of solid nitrogen and the bath can lasts for around 3 weeks.

In addition, a heater with precise temperature controller allows sample temperature adjustment at the expense of extra consumption of cryogens. The achievable temperature range depends on the base temperature and the latent heat. The counter heating function enables various-temperature experiments in our system.

2.3.3 Tip preparation and characterization

Tip preparation and characterization is one of the key issues in STM experiments, which was recognized by Binnig and Rohrer from the beginning of their experimentation [99]. We use electrochemically etched tungsten(W) tips for actual measurement. The basic setup is shown in Fig. 2.7(a). A piece of W wire with a diameter of 0.25 mm
Figure 2.8: Images of tip etching process. (a) Image of electrochemical etching setup. The straight thin wire is a tungsten wire with diameter of 0.25 mm and the outer ring is made of stainless steel. The liquid film in the ring is NaOH solution. A positive DC voltage (5 − 7 V) is applied on the tungsten wire. (b) Image of an etched tungsten tip taken under an optic microscope. (c) Image of tunneling junction of the tip and Au(111) surface.

is placed through a liquid film of 2 M/L NaOH solution, which is formed by dipping a stainless steel ring in a beaker full of the solution. Next a DC voltage (5 − 10 V) is applied between the two electrodes: the W wire as anode and the metal ring as cathode to trigger the electrochemical etching process. The overall reaction is

\[ \text{W}(s) + 2 \text{OH}^- + 2 \text{H}_2\text{O} \rightarrow \text{WO}_4^{2-} + 3 \text{H}_2(\text{g}) \]

The etching typically takes 10-15 minutes. After the W wire breaks, the tip which is the lower part of W wire is thoroughly rinsed with deionized water and alcohol to remove the residual NaOH from the tip surface. Fig. 2.7(b) shows an image of an etched W tip taken under optical microscope.

A W tip made by electrochemical etching is seldom good enough for scanning immediately, since the tip surface is covered by tungsten oxides and various contaminations and the arrangement of the apex atoms may not generate atomic resolution or reproducible tunneling spectra. Therefore, the tips are loaded into STM chamber quickly for in situ tip treatment before use [87].

Au(111) surface is used for in situ tip preparation and tip characterization as the properties of Au(111) surface is well known in prior STM studies[100]. A high-field emission treatment is first applied on a fresh tip. The tip is shortened by several
micrometers so that the pure tungsten is exposed. The tip sharpening and density of states modification are subsequently achieved by repeated controlled collision on the Au(111) surface. After each collision, the tip is characterized on Au(111) until it can reproduce the standard spectra shown in Fig. 2.8(a), which was measured with a tip with flat density of states. Meanwhile, the qualified tip should also be sharp and the geometry of its apex be circularly symmetric. Fig. 2.8(b) shows a topographic image taken by a sharp and good tip. One tip can be used for 1 – 4 weeks before it takes too long to restore a good condition.

Figure 2.9: Tip characterization on Au(111) surface. (a) Duplicate of topographic image in Fig.2.6(a). (b) Topographic image taken by a sharp tip with a good shape. The adatoms are clear and circularly symmetric. (c) Standard \( \frac{dI}{dV} \) spectra on Au(111) surface. The tip which can reproduce these spectra has roughly flat DOS of the tip.

### 2.3.4 Sample preparation

For cleavable crystal materials, the sample is first attached to a sample holder with conductive epoxy H20E. Next, a cover glass and an aluminum bar are glued on top of sample in order. In the UHV chamber, we in situ cleave the sample by knocking off the aluminum bar. The cover glass is gone with the aluminum bar so that the
sample is cleaved in the middle, exposing a clean surface. The cleaved sample is then transferred into the scan head for measurement.

For film sample grown by MBE method, the surface treatment is performed in the preparation chamber. In order to protect the surface from contamination got in the air, a protection capping layer of another material is grown on top of the material of interest. The material of the capped layer usually has a high vapor pressure and is easy to sublimate. In our preparation chamber, we anneal the sample to sublimate the capping layer so that the pristine surface of interest is restored in the UHV environment. For example, an successful application of this method has been demonstrated on topological insulator Bi$_2$Se$_3$ films with a capped amorphous protection layer [101].
Chapter 3

Effect of Defects on Bulk Conduction of Topological Insulator Bi$_2$Se$_3$

3.1 Identification and Effective suppression of native defects in Bi$_2$Se$_3$ crystals

3.1.1 Motivation

Many exotic quantum phenomena emerge from the topological surface states with symmetry breaking [102, 41, 42]. To experimentally realize these fascinating phenomena, the TI materials need to be intrinsic, i.e., $E_F$ is located in the band gap, in which case the transport is dominated by the topological surface states instead of bulk states. However, many TIs are doped semiconductor because of the existence of native defects [8]. It impedes the progress and potential applications of TIs. Intensive efforts have been made to suppress this conduction from the bulk, but they introduce potential fluctuation or disorder [103], which is detrimental for the mobility of the Dirac surface states. One of the biggest challenges is the lack of clear identification and characterization of native defects, which is crucial for optimizing synthesis conditions and device fabrications. It is a difficult task to directly visualize and identify defects experimentally. Usually, a combination of first-principle calculation and experiment is a necessity to understand and control defect-associated properties [72, 104]. Even with this collaboration, the evidence supporting a defect model is indirect. STM is one powerful technique to directly address this issue [103, 105, 106]. As shown in the prior studies on Sb$_2$Te$_3$ thin films [107], the atomic resolution STM images are crucial
to identifying native defects and obtaining high-quality samples via optimization.

This section, based on the work published in Ref. [108], is dedicated to the STM studies on Bi$_2$Se$_3$, one of the most promising 3D TI system because of its relatively large band gap ($\sim 0.35$ eV) and a simple surface band structure. Nominal Bi$_2$Se$_3$ single crystals are always electron doped semiconductors due to the high density of native defects. Prior studies suggested the dominant donors in Bi$_2$Se$_3$ were Se vacancies (denoted as V$_{\text{Se}}$ in this chapter) [109, 110], but there has been no clear identification of V$_{\text{Se}}$ until now [103, 105, 111, 112]. In this work, comparison between STM images and theoretically simulated STM images allows one to unambiguously identify the native defects and the corresponding densities, including Bi$_{\text{Se}}$, V$_{\text{Se}}$, Se interstitial defects (denoted as Se$_i$). The dominant V$_{\text{Se}}$ defects are located in the middle layers, which are energetically unfavorable positions. Along with the existence of Se interstitial defects, they demonstrate the significance of kinetics for defect formation in Bi$_2$Se$_3$ single crystals. Moreover, the STS mapping shows that the V$_{\text{Se}}$ defects are responsible for the local potential fluctuation. With delicate control of stoichiometry and synthesis conditions, high quality Bi$_2$Se$_3$ single crystals with $E_F$ being 60 meV below the CBM can be obtained, approaching the intrinsic semiconductor limit without compensation doping.

### 3.1.2 Identifications of native defects

Fig. 3.1(a) shows an atomically resolved topographic image of cleaved surface of nominal Bi$_2$Se$_3$ with slight Se deficiency. The sample bias is $-0.7$ V, at which the atomic corrugation is usually pronounced. The subatomic resolution allows clear identification of atomic positions as illustrated in Figs. 3.1(b-c). Two kinds of defects at Se sites are observable: depressions (green) and protrusions (blue) marked in Fig. 3.1(a). This agrees well with the earlier first principle calculations that low formation energy defects are V$_{\text{Se}}$ and Bi$_{\text{Se}}$ [109, 110]. Prior STS measurements of Bi$_{\text{Se}}$ show a defect state manifested as a LDOS peak near the VBM [105, 106, 110]. Herein,
$dI/dV$ data of protrusions all show pronounced LDOS peak associated with Bi$_{Se}$, while no anomaly in $dI/dV$ spectra of depressions is observed [108]. Therefore, one can assign protrusion defects as Bi$_{Se}$ and depressions as V$_{Se}$, which are summarized in Fig. 3.2. The high resolution topographic data provides clear identification of V$_{Se}$ in all possible depths in the topmost QL of Bi$_2$Se$_3$, which is corroborated by the first principle simulations.

Figure 3.1: (a) Atomically resolved STM image of (001) surface of nominal Bi$_2$Se$_3$. Tunneling parameter is $U = 0.7$ V, $I = 0.2$ nA. Green circle, triangle, and squares mark a V$_{Se}$ at the 1A, 3C, and 5B sites, respectively. The blue circle and square mark a Bi$_{Se}$ antisite at the 1A and 6C sites. The black square marks a triangular defect (Se interstitial defect) at the A site. See Fig. 3.2 for details. (b) Schematic of the triangular lattice and definition of the A, B, and C sites. (c) Definition of atomic sites (1A, 2B, 3C, etc.) in the crystal structure of Bi$_2$Se$_3$. (d) $dI/dV$ spectrum of nominal Bi$_2$Se$_3$. The Dirac point energy ($E_D$) is $\sim 340$ meV. Adapted from Ref. [108].

The dominant defects are V$_{Se}$ at 3C sites. The estimated concentration is $\sim 3 \times 10^{19}$ cm$^{-3}$, consistent with the $dI/dV$ spectrum [Fig. 3.1(d)] with $E_F \sim 140$ meV above the CBM. Another prominent V$_{Se}$ defect emerges at 1A site as a depression of a single atom. A more subtle V$_{Se}$ [green squares in Fig. 3.1(a)] is also visible, which is at 5B site. They are crystallographically equivalent, which is indeed consistent with the result that their concentrations are statistically the same. Note that V$_{Se}$ at 3C
site has never been reported in prior studies, probably because of the weak atomic resolution. The kind of defect is unexpected because of its high formation energy. Its present may be because the $V_{Se}$ defects at 3C site are formed at high temperature and trapped kinetically during the cooling process. Beside the $Bi_{Se}$ defects at 5B and 6C sites which have been identified in earlier STM studies, $Bi_{Se}$ at 1A site is also identified, which has not been reported before. This is possible because the pronounced corrugation makes it easily confused with surface absorbed atoms [108].

![Image](image.png)

Figure 3.2: Experimental (left) and simulated (right) STM images of native defects in Bi$_2$Se$_3$. (a-c) STM images of $V_{Se}$ at 1A, 3C, and 5B sites measured with $-0.7$ V. (d-f) STM images of $Bi_{Se}$ antisites at 1A, 5B, and 6C sites measured with $-0.6$ V. (g-h) STM images of an intercalated Se at $-0.7$ V and $+0.5$ V, respectively. The grey-scale images on the right side are the corresponding simulated STM images. Adapted from Ref. [108].

Previous STM studies associated triangular defects observed at positive bias with $V_{Se}$ [105, 113, 81]. This type of defect is also observed, as shown in Fig. 3.2(h). The atomically resolved topographic image indicates that it sits at the A site $\sim 5.5$ atomic layers beneath the surface. Its density is much lower than that of $V_{Se}$ and increases in Bi$_2$Se$_3$ grown in the Se rich condition. These observation indicates that this triangular defect is not $V_{Se}$ defects, and instead it is likely to be Se interstitial defect sitting in the vdW gap between QLs.
3.1.3 Microscopic fluctuation of potential and Dirac point energy

$V_{Se}$ defects are charge defects and act as donors, which influence the local potential. Prior works show fluctuation of the local potential and Dirac point energy ($E_D$) of the Dirac surfaces state in doped and undoped Bi$_2$Se$_3$ [103, 105], but the microscopic origin has not been addressed. In this work, the STM results demonstrate the responsibility of $V_{Se}$ for the local fluctuation of potential. Fig. 3.3(a) shows a representative topographic image of randomly distributed $V_{Se}$ defects in Se deficient Bi$_2$Se$_3$. Spectroscopic grid mapping measurement makes it possible to estimate and local band shift and the $E_D$ by tracking the kink marked in Fig. 3.1(d). Fig. 3.3(b) and (c) show the spatial fluctuation of $E_D$ and the $dI/dV$ map taken at $-500$ meV reflecting the potential fluctuation patterns, respectively. One can clearly observe a positive correlation between local defect concentration and the local $E_D$, and a negative correlation between the local defect concentration and the local potential [108]. Thus, the significant amount of $V_{Se}$ defects not only cause the n-type bulk conduction, but also result in the microscopic fluctuation of potential and Dirac point energy, which could be harmful for the topological transport properties.
3.1.4 Obtaining intrinsic TI by synthesis optimization

As the native defects are clearly identified, one can correlate the defect population with growth conditions to gain some insights on the material synthesis. Fig. 3.4(c) shows a plot of defect density ($n$) vs $E_D$ measured on multiple Bi$_2$Se$_3$ crystal samples. $E_D$ increases systematically with decreasing $n$ of V$_{Se}$, which agrees well with estimation of carrier density from a simple parabolic band [114, 115]. Moreover, the reduction of density of V$_{Se}$ defects is associated with increasing fraction of Se in the starting materials. However, the STM results show that the Se-rich condition would leads to a substantial increase of Se interstitial defects instead of Se$_{Bi}$ as predicted by thermodynamics [109]. The STM results show that the Se interstitial defects are
also donors [108]. It is consistent with the result that Se-rich crystals are also n-type doped, as shown in the sample with $E_D \sim -240$ meV.

With delicate control of the stoichiometry of Bi$_2$Se$_3$ crystal (Bi:Se = 2:3), the tendency of forming V$_{Se}$ and Se$_i$ is greatly suppressed. Crystals were cooled to room temperature slowly to avoid formation of kinetically trapped defects. Fig. 3.4(d) shows a representative topographic image of the best sample, in which the defect concentration is very low ($< 10^{18}$ cm$^{-3}$) with negligible potential fluctuation. Furthermore, the $dI/dV$ spectrum taken on this sample [inset of Fig. 3.4(d)] shows that $E_D$ is $-145$ meV below $E_F$, which indicates the Fermi level is $\sim 60$ meV below the CBM.

Figure 3.4: (a-b) Illustration of $E_F$ relative to the band structure in typical or best Bi$_2$Se$_3$ samples. (c) A diagram of $n$ vs $E_D$ in various Bi$_2$Se$_3$ crystals with various growth conditions. (d) Representative topographic image of Bi$_2$Se$_3$ with extremely low defect density. Inset: corresponding $dI/dV$ spectrum showing that $E_F$ is below CBM. Adapted from Ref. [108].
In conclusion, unambiguous identification of the prominent native defects, especially V$_{Se}$, in Bi$_2$Se$_3$ single crystals was achieved by combining STM/STS experiments and first principles simulations. The results indicate that the concentrations of native defects do not reflect their thermodynamic formation energies. Instead, they are greatly affected by the kinetics of synthesis. This is valid not only for the dominant V$_{Se}$ in the middle layer, but also for the Se interstitial defects sitting in the vdW gap between QLs and for the absence of Se$_{Bi}$. These findings show the significance of both kinetic control of defect formation and strict stoichiometry in the growth process, which lead to improved synthesis of high quality single crystals with low defect density and minimal potential fluctuation. The best sample of Bi$_2$Se$_3$ with $E_F$ below the CBM suggests a viable route toward the intrinsic limit of TIs for potential applications of the topological surface states.
3.2 Calcium doping in Bi$_2$Se$_3$ thin films

This section is based on the work published in Jisoo Moon, Nikesh Koirala, Maryam Salehi, Wenhan Zhang et al. Nano Lett. 2018, 18, 820826 (Ref. [116]).

3.2.1 Motivation

Hole-doping has always been a challenging task in Bi$_2$Se$_3$ [109, 105]. The bulk states have a strong tendency to be n-type in the presence of native defects such as Se vacancies, as demonstrated in the prior section of this chapter and other works [105, 8]. A common approach of tuning the carrier types is compensation doping the material with the acceptor dopants. In bulk Bi$_2$Se$_3$ crystals, the dominant carrier type can be converted from n-type to p-type by compensation dopants such as Ca, Mn or Ti [117, 118, 119, 120, 121, 122]. Fig. 3.5 demonstrated a shift of the Fermi level between electron-doped Bi$_2$Se$_3$ crystal and hole-doped Bi$_{1.98}$Ca$_{0.02}$Se$_3$ crystals in the $dI/dV$ measurements, which is adapted from Ref. [118]. In Bi$_{1.98}$Ca$_{0.02}$Se$_3$, $E_D = E_F + 0.1$ eV, indicating that the Fermi level is close to the VBM. On the other hand, such a compensation doping scheme has never been realized successfully in the Bi$_2$Se$_3$ thin films. Several common compensation dopants such as Zn, Mg has been tried, but none of them led to p-type Bi$_2$Se$_3$ thin films. There is no consensus on the origin of the different doping efficiency. It may result from the different growth conditions such as growth temperature, as the thin films are generally synthesized at a lower temperature than the crystals. It may also associated with thickness of the material, because some prior studies suggest that Bi$_2$Se$_3$ flakes made by Scatch type method can maintain p-type only when it is relatively thick (e.g., $>\sim 150$ nm) [123]. It would be a significant breakthrough to solve the p-doping mystery and achieve hole-doped Bi$_2$Se$_3$ thin films in several tens or even several QLs. To achieve this, thorough investigation of dopants and this influence on the sample properties is necessary. STM is a powerful tool to visualize the compensation dopants with the atomic resolution as well as
characterize the properties of the films such as sample quality, defect concentration and distribution. All of these factors can greatly affect the electronic properties of Bi$_2$Se$_3$ thin films. To address this, we systematically studied a series of thin films with different compensation schemes with STM.

![Figure 3.5: (a) Spatially averaged $dI/dV$ spectra showing the shift of $E_F$ between n-type Bi$_2$Se$_3$ and p-type Bi$_{1.98}$Ca$_{0.02}$Se$_3$. (b) STM topographic image at $Bias = +1$ V showing triangular-shaped defects observed at various intensities, indicating they are located in different layers beneath the surface. Adapted from Ref. [118].](image)

### 3.2.2 Thin film synthesis and preparation

Obtaining p-type Ca-doped Bi$_2$Se$_3$ thin films is not a trivial task. Initial experiment results show that if Bi$_2$Se$_3$ films are directly grown on Al$_2$O$_3$ (0001) surface, which is commonly used for TI film growth, without any buffer layer or protection layer, the films persist n-type regardless of Ca doping level and sample thickness [116]. Subsequent studies show that previous failure of compensation doping mainly results from two factors: (1) extra n-type dopant from the top film surface due to air exposure [124] and (2) the high interstitial defect density at the interface between film and the substrate. The thin film samples utilized in this project were grown with MBE method by our collaborators Seongshik Oh’s group. They overcame those limitations by growing the TI film on top of a buffer layer made of 20 QL (Bi$_{0.5}$In$_{0.5}$)$_2$Se$_3$ and
protecting its surface with a Se capping layer. Once the buffer layer and Se capping layer are applied, the p-type Bi$_2$Se$_3$ can be achieved down to 6 QL.

Unlike transport measurement, the STM experiment is conducted in the UHV environment, so there is no surface contamination at the time of STM measurement. Yet the films still need protection from air exposure when being ex situ transferred from MBE chamber to the STM chamber. The Se capping layer can satisfactorily serve this purpose. It is then evaporated following the procedure described in Chapter 2.3.4 to recover the pristine surfaces of Ca-doped Bi$_2$Se$_3$ thin films before STM measurements.

### 3.2.3 Topography and identification of Ca defect

The (Bi$_{1-x}$Ca$_x$)$_2$Se$_3$ samples we measured are all 20 QL thick. The nominal Ca doping level $x$ varies from 0 to 12%. Fig. 3.6 shows the representative topographic images in a large scale ($> 150 \times 150$ nm$^2$). The crystalline quality of the films is positively associated with the typical size of terraces. When $x \leq 2\%$, the sample quality is comparable with that of the pure Bi$_2$Se$_3$ thin film, where the typical terrace size is $> 100$ nm. Yet as $x \geq 6\%$, the size of terraces greatly shrinks: $\sim 50$ nm for 6% and $< 50$ nm for 12%.

Ideally the dominant defect in the (Bi$_{1-x}$Ca$_x$)$_2$Se$_3$ thin films is supposed to be Ca atoms substituting Bi sites, denoted as Ca$_{Bi}$. They emerge at either 2B or 4A sites in the topmost QL. In practice, other species of defects may exist. E.g., there may commonly exist Indium defects, which diffuse from the (Bi$_{0.5}$In$_{0.5}$)$_2$Se$_3$ buffer layer. Similar to Ca, In also occupies the Bi site at 2B or 4A sites. At the negative bias, the defect shapes of In and Ca are similar. E.g., at $-0.6$ V, both Ca(2B) and In(2B) appears like dark triangular suppression, except that Ca(2B) is surrounded by a bright border, as shown in Figs. 3.7(a-c). At positive bias, Ca and In appear greatly different. Ca(2B) appears as a clover-like suppression at $+1$ V, while In(2B) appears still a triangular suppression, as shown in Fig. 3.7(c). The difference between
Figure 3.6: Large scale topographic images of $(\text{Bi}_{1-x}\text{Ca}_x)\text{Se}_3$ thin films of 20 QLs with nominal $x$ varying from 0 to 12%. As the Ca concentration increases, the typical size of terraces reduces from $\sim 100$ nm to $\sim 10$ nm. It indicates the quality of sample becomes lower and lower.

In and Ca defects at 4A sites is similar to those at 2B sites. Fig. 3.7(d) shows more detailed bias-dependent characterization of Ca defects. Being able to identify Ca defects at the atomic scale, we can compute the real Ca concentration. In the $x = 2\%$ sample, the calculated Ca concentration in the second atomic layer (2B site) from topographic image is $\sim 0.1\%$ and that in the fourth atomic layer (4A site) is $\sim 0.15\%$, both of which are far below the nominal Ca doping level. This may be caused by the inhomogeneous distribution of Ca at different depths from the surface occurring during the growth. This is consistent with the fact that the Ca density at 4A site is higher than that at 2B site.
Figure 3.7: Identification of Ca defect in (Bi$_{1-x}$Ca$_x$)$_2$Se$_3$ thin films. (a-b) Topographic images taken in the different regions of (Bi$_{1-x}$Ca$_x$)$_2$Se$_3$ thin films presenting Ca defects in the second and fourth atomic layer. They are Ca atoms substituting Bi sites. The sample bias is −0.6 V. (c) Indium defects in Bi$_2$Se$_3$, which is another commonly seen defects in (Bi$_{1-x}$Ca$_x$)$_2$Se$_3$ thin films. The images show the bias-dependent defect shapes of In. (d) Bias-dependent topographic images of Ca defects. Ca and In defects have different appearances at both −0.6 V and +1 V. Ca(2B), for example, shows extra bright border compared with In(2B) defects at −0.6 V, and changes its shape at +1 V to a clover with 3 petals. By contrast, the appearance of In(2B) changes little.

3.2.4 Tuning bulk carrier by Ca dopants

Next, we investigated the bulk carrier types for a range of films grown on buffer layers via Hall effect measurements. Let’s focus on the 20 QI samples, as shown by the second row in Fig. 3.8(a). As the Ca concentration increases and compensates for the intrinsic n-type carriers, the n-type carrier density reduces, manifested as the increasing negative slope of Hall resistance $R_{xy}(B)$. When nominal Ca concentration reaches 0.13%, the system passes through a nonlinear n-p mixed regime. With even higher Ca concentration, the film becomes p-type, appearing as a positive slope. This behavior is universal in films with various thicknesses. Thinner films possess
higher critical Ca concentration of n-p transition, which shows that the counter-doping become more difficult and requires a higher level of Ca doping as the films get thinner. This suggests that the majority of n-type defects still originates from the interface instead of the bulk of the films.

Notably, the (Bi$_{1-x}$Ca$_x$)$_2$Se$_3$ thin films become n-type again with further increase of Ca doping level (> 4.4%). This is because the high level of Ca doping would degrade the morphology of the thin films. As discussed in the prior section, the terrace size shown in the topographic images greatly shrinks as $x \geq 6.0\%$, which indicates the degradation of the morphology. The change of morphology is consistent with the n-type nature of heavily Ca-doped Bi$_2$Se$_3$ thin films. The average $dI/dV$ spectra taken on (Bi$_{1-x}$Ca$_x$)$_2$Se$_3$ thin films [Fig. 3.9] corroborate this re-entrant n-type behavior. As shown, when $x \leq 6.0\%$, $E_F$ falls in the range ($E_D + 0.15$ eV, $E_D + 0.2$ eV). However, as $x = 12\%$, $E_F$ shifts to as high as $E_D + 0.37$ eV, being well above the CBM, which indicates the (Bi$_{1-x}$Ca$_x$)$_2$Se$_3$ film become electron-doped again.
Figure 3.8: Hall resistance study for n- and p-type Bi$_2$Se$_3$ thin films. $R_{xy}(B)$ data vs Ca density and thickness for Ca-doped Bi$_2$Se$_3$ films with the buffer and the Se capping layers. n-type (negative slope) and p-type (positive slope) curves are colored as red and blue, respectively, and the nonlinear, n-p mixed curves are colored as pink. As Ca concentration increases, all the films transition from n- to p-type through np mixed regime, and then eventually become n-type again except for the 6 QL film, which becomes insulating, instead. (b) A phase diagram for the carrier type in the thickness and Ca concentration space: n, np mixed, and p regime are depicted as red, pink, and blue squares, respectively. Note that the phase space for the p regime shrinks as the film gets thin. (c) A cartoon showing the common trend of $R_{xy}(B)$ depending on Ca concentration for all thicknesses. (i) Bi$_2$Se$_3$ is naturally n-type without Ca dopants. (ii) As Ca doping level increases, the (n-type) sheet carrier density gradually decreases, resulting in increased negative slope of the $R_{xy}(B)$ curve. (iii,iv) With more Ca doping, the slope changes from negative (n-type) to positive (p-type) passing through a nonlinear np mixed regime. Adapted from Ref. [116].
Figure 3.9: $dI/dV$ spectra of $(Bi_{1-x}Ca_x)_{2}Se_3$ thin films with various $x$. $E_D$ of the $x \leq 6\%$ film samples falls in the range $(E_F - 0.2 \text{ eV}, E_F - 0.15 \text{ eV})$, while $E_D$ of $x = 12\%$ is far below the Fermi level: $E_D = E_F - 0.37 \text{ eV}$.

3.2.5 Summary

In conclusion, this work shows that the major challenges of hole doping Bi$_2$Se$_3$ thin films in prior efforts are (1) high density of interstitial defects at the interface between film and substrate and (2) neutralization of the dopant due to the air exposure. Our experiments demonstrate an applicable approach to overcome them and realize p-type Bi$_2$Se$_3$ thin films with Ca doping by carefully choosing the buffer layer and protecting capping layer. With STM, we are able to characterize the Ca defects in Bi$_2$Se$_3$ thin films and study their impact on the crystal quality reflected by large-scale morphology of sample surface. Our STM results show that the thin films degrade when they are heavily doped with Ca. Such film degradation is likely responsible for the re-entrance to n-type regime at a high level of Ca doping observed in the transport measurements. The solution to the hole-doping problem of Bi$_2$Se$_3$ thin films may serve as a stepping stone of future development of topological quantum electronic devices.
Chapter 4

Topological Phase Transition in \( (\text{Bi}_{1-x} \text{In}_x)\text{Se}_3 \) with Nanoscale Inhomogeneity

This chapter is based on the work published in Zhang, Wenhan et al. *Nano letters* 2018, 18, 4, 2677-2682 (Ref. [125]).

4.1 Motivation

The existence of defects or impurities often leads to electronic or chemical disorders, which are inevitably present in any functional materials or physical system. They have important impact on many areas of physics, including condensed-matter physics [2], photonics [126, 127], and cold atoms [128]. E.g., quench disorders induce both frustration and randomness in doped magnets, the key ingredients of spin glass physics [129]. Quenched disorders due to chemical doping are associated with the observed nanoscale inhomogeneity in high \( T_c \) cuprates [78, 79] and CMR manganites [130]. Strong disorders can also localize itinerant electrons [131], which is critical for many appealing phenomena such as metal insulator transition and quantum Hall effects [15, 132, 133]. However, the realization of quantum Hall effect requires high magnetic field, a hurdle for its broader applications. Thus, physicists have been searching solution for QAHE without magnetic field. It leads to conception of QAHE [16] and QSHE [19, 20], which eventually lead to the birth of 3D TI [5, 7, 23, 134].

In 3D TI, the non-trivial topology of band structure is caused by the band inversion due to strong SOC [5, 7, 23, 134, 135]. The change of topology class at the interface between topological and normal insulators ensures the existence of metallic
Dirac surface states [28, 29, 31, 25, 27, 136]. Similarly, the topological distinction also enforces a zero band gap Dirac semimetal state or Weyl semimetal for spatially uniform topological phase transition (TPT). In theory, TPT can be induced by gradual change of average SOC strength via chemical doping, and has been experimentally established in TlBi(S_{1-x}Se_x)_2 and (Bi_{1-x}In_x)_2Se_3 via spatially averaged measurements [137, 138, 139, 140, 141, 142]. Because of topological stability, the band inversion is robust against weak disorders. The impact of strong disorders is quite rich. On one hand, strong lattice disorder can drive a TI into a normal insulator (NI) [143]. On the other hand, disorders could transform a metal with strong SOC into a topological Anderson insulator [144, 145, 146], though more elaborate theoretical analysis suggests that it is adiabatically connected to intrinsic TI at the clean limit [147]. Although TPT has been studied in few systems, the impact of disorders due to chemical doping has not been addressed. Furthermore, Lou et al. reported a mysterious sudden band gap closure across TPT in In doped Bi_2Se_3 using ARPES [141].

In this chapter, I present systematic high-resolution STM/STS studies on single crystals (Bi_{1-x}In_x)_2Se_3, where x varies from 0.2% to 10.8%. To our surprise, no band gap closing and reopening was observed across the TPT (x_c \approx 6%). Instead, the average band gap gradually increases across the transition. STS imaging reveals that In defects are extremely effective on changing topological properties locally, i.e. suppressing the topological surface states (TSS) and increasing band gap. The characteristic length of suppression is comparable with the decay length of TSS in Bi_2Se_3 (\sim 1 \text{ nm}), suggesting that individual In defects are effectively point NIs. The suppression is strongly enhanced in neighboring In defects, resulting in nanoscale mixture of TI and NI regions with proliferation of TSS inside the bulk across the TPT. The observation of TPT with nanoscale inhomogeneity will not only promote future investigations on the impact of disorders on TPT, but also open a door to optical sensing by harnessing percolative network of TSS.
4.2 Experimental and computational methods

This study was conducted on a series of (Bi$_{1-x}$In$_x$)$_2$Se$_3$ high-quality single crystals with various In concentrations ($x$) via self-flux method. They were synthesized by Prof. Sang-Wook Cheong’s group at Rutgers. Our Omicron LT-STM with base pressure of $1 \times 10^{-11}$ mbar was used for STM/STS measurements. We prepared the tip and samples following the operations described in Chapter 2.3. All STM data were taken at 4.8 K. The spectroscopy mapping measurements were performed with standard lock-in technique with modulation frequency $f = 455$ Hz and amplitude $V_{\text{mod}} = 5 - 10$ mV. To supplement the experimental findings, our collaborators Mingxing Chen and Zhicheng Zhong carried out the density functional theory (DFT) calculations using the Vienna *ab initio* Simulation Package [148, 149].

4.3 Evolution of energy band gap across the topological phase transition

4.3.1 Topographic images

Figure 4.1(a) shows the side view schematic of one QL of (Bi$_{1-x}$In$_x$)$_2$Se$_3$ [28, 34]. In atoms (red) preferentially occupy the Bi sites (blue), so they are observed in either the second or fourth atomic layer from surface[Fig. 4.1(b)]. Atomically resolved topographic images were obtained in all the samples. The representative STM images are shown in Fig. 4.2.
Figure 4.1: Topographic images of In defects in the second and fourth layers of the topmost QL of Bi$_2$Se$_3$. (a) Schematic of crystal structure of 1 QL of (Bi$_{1-x}$In$_x$)$_2$Se$_3$. Se, Bi and In atoms are denoted by green/yellow, blue and red spheres, respectively. (b) Atomically-resolved topographic images showing representative In defects in the second and fourth atomic layer (marked by red circles).
Figure 4.2: Atomically-resolved topographic images of the samples with various In concentrations: (a) $x = 0.2\%$, (b) $x = 2.1\%$, (c) $x = 4.8\%$, (d) $x = 6.1\%$, (e) $x = 9.0\%$ and (f) $x = 10.8\%$. The tunneling condition is $V_B = -0.6$ V, $I = 1$ nA. The scale bars represent 5 nm.

4.3.2 Average $dI/dV$ spectra and topological surface states

Fig. 4.3(a) shows the average $dI/dV$ spectra ($-0.6$ to $0.4$ eV) of each sample (offset vertically for clarity). All the spectra are obtained by averaging over 6000 single-point spectra in the sampling areas typically over $225 \text{ nm}^2$. The reference levels are marked by black dashed lines. Tunneling spectrum $dI/dV$ is proportional to the LDOS. Due to the presence of TSS, the LDOS within the band gap is not zero. Fig. 4.3(b) shows the zoom-in $dI/dV$ spectra inside the band gap. The Dirac point and the linear LDOS of TSS are clearly resolved in the $dI/dV$ spectra for $x \leq 6.1\%$, but are less visible for $x > 6.1\%$, indicating that the critical In concentration ($x_c$) of TPT is $\sim 6\%$, in good agreement with prior transport and optical spectroscopy studies [139, 140]. Interestingly, the spectral weight of Dirac point gradually decreases as $x$ increases.
4.3.3 Estimation of band edges via linear fitting on average \(dI/dV\) spectrum

It is meaningful to examine how the average band gap evolves as the In concentration increases. Although it is not straightforward to determine the band gap \(\Delta\) using STS in the presence of TSS, the slope change of \(dI/dV\) curves near band edges provides a reasonable criterion for estimation of conduction band minimum (CBM) and valence band maximum (VBM). We fitted the band edges in the \(dI/dV\) spectra [Fig. 4.3(a)] with linear functions. The band edges are defined by the intercepts with the horizontal axis of the best linearly fitted \(dI/dV\) near band edges. To find out the optimal range for linear fitting, the \(R^2\) values are computed with a fixed fitting length but different fitting centers. The results with the largest \(R^2\) values are chosen.

In the average \(dI/dV\) spectrum of \(x = 0.2\%\) sample, for example, the dependence
Figure 4.4: (a) \( R^2 \) value as a function of various fitting ranges on the average \( dI/dV \) spectrum of \( x = 0.2\% \) samples. Purple and red color are denoted to the fitting length of 0.1 eV and 0.2 eV, respectively. (b)-(c) Zoom-in graphs of purple and red boxes in (a). The black arrows indicate the standard for linear fitting of valence band and conduction band, respectively, where \( R^2 \) is maximized. (d) Linear fitting of all the samples. Arrows indicate the optimized fitting center when estimating VBM. (e) Results of linear fitting CBM. (f)-(g) 2 examples of band edge estimation on single-point \( dI/dV \) spectra. Yellow (blue) lines are denoted to the CBM (VBM) estimation.

of \( R^2 \) on the fitting center is shown in Fig. 4.4(a). Here, we apply a fitting length of 0.1 eV on VBM and 0.2 eV on CBM, because the \( dI/dV \) spectra of conduction band is less linear than valence band. Fig. 4.4(b) and (c) are zoom-in figures of violet and red dash boxes in Fig. 4.4(a). They display the dependence of \( R^2 \) on fitting centers near VBM and CBM, respectively. The optimal fitting centers of VBM and CBM are indicated by the black arrows \([-0.39 \text{ eV in (b)} \text{ and } 0.3 \text{ eV in (c)}]\), where the \( R^2 \) is maximum. Therefore, the optimum fitting ranges of the sample \( x = 0.2\% \) are \((-0.44 \text{ eV, } -0.34 \text{ eV})\) for the VBM and \((0.2 \text{ eV, } 0.4 \text{ eV})\) for the CBM. The same criterion is applied to the average \( dI/dV \) spectra of other samples. The fitting centers of VBM and CBM of different samples are given in Fig. 4.4(d-e), respectively. Fig. 4.4(f-g) depict the band edge fitting on two example single \( dI/dV \) curves. The effectiveness of this method is visually confirmed by the good separation of bulk band
and in-gap topological surface states. The comprehensive results of linear fitting of all samples are shown in Table 4.1 and with the black solid lines in Fig. 4.5.

<table>
<thead>
<tr>
<th>$x$</th>
<th>VB Fitting Range (eV)</th>
<th>VBM (eV)</th>
<th>CB Fitting Range (eV)</th>
<th>CBM (eV)</th>
<th>Band gap (eV)</th>
</tr>
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<tr>
<td>0.2%</td>
<td>(-0.44, -0.34)</td>
<td>-0.286</td>
<td>(0.2, 0.4)</td>
<td>0.103</td>
<td>0.389</td>
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<td>2.1%</td>
<td>(-0.46, -0.36)</td>
<td>-0.319</td>
<td>(0.2, 0.4)</td>
<td>0.112</td>
<td>0.431</td>
</tr>
<tr>
<td>4.8%</td>
<td>(-0.48, -0.38)</td>
<td>-0.342</td>
<td>(0.2, 0.4)</td>
<td>0.115</td>
<td>0.457</td>
</tr>
<tr>
<td>6.1%</td>
<td>(-0.54, -0.44)</td>
<td>-0.409</td>
<td>(0.12, 0.32)</td>
<td>0.055</td>
<td>0.464</td>
</tr>
<tr>
<td>9.0%</td>
<td>(-0.55, -0.45)</td>
<td>-0.430</td>
<td>(0.19, 0.39)</td>
<td>0.096</td>
<td>0.526</td>
</tr>
<tr>
<td>10.8%</td>
<td>(-0.58, -0.48)</td>
<td>-0.455</td>
<td>(0.2, 0.4)</td>
<td>0.085</td>
<td>0.540</td>
</tr>
</tbody>
</table>

Figure 4.5: Duplicate of Fig. 4.3(a) with estimated band gaps. Black lines indicate the estimation of band edges.

4.3.4 Estimated band gap via $d^2I/dV^2$ spectra

In order to solidify the estimation of average band gap, we also used a different criterion (i.e. “kinks” in the $d^2I/dV^2$ curves [150]) and obtained similar results. This supports the aforementioned linear-fitting method. The LDOS of the TSS is only “visible” within the band gap in the tunneling spectroscopy, because that of the bulk
states is a lot higher. Therefore, the CBM and VBM are expected to appear as the kinks in the $d^2I/dV^2$ spectrum.

The red curve in Fig. 4.6(a) shows the $d^2I/dV^2$ spectrum. The kinks indicated by the crossings of black dash lines correspond to the CBM and the VBM. The similar analysis was also applied to other compositions. The band edges and band gaps obtained with this method are in good agreement with those estimated by the linear-fitting method, as shown in Fig. 4.6(b).

![Figure 4.6](image)

Figure 4.6: (a) $dI/dV$ (blue) and the corresponding $d^2I/dV^2$ (red) taken on the sample of $x = 0.2\%$. The VBM and CBM are marked by black arrows. (b) The band gap estimated on $d^2I/dV^2$ spectra and the average band gap from linear fitting as functions of $x$.

4.3.5 Summary of In concentration dependence of band edges, band gap and Dirac energy

Fig. 4.7(a) shows a summary of the estimated CBM and VBM, and the Dirac energy $E_D$ as functions of $x$. The CBM remains almost unchanged as the In concentration increases while the VBM gradually shifts down. As shown in Fig. 4.7(b), this results in a monotonic increase of band gap toward that of In$_2$Se$_3$ ($\Delta \sim 1.3$ eV) [139]. Such behavior is in apparent conflict with the aforementioned picture of band closing.
and reopening, but is consistent with recent ARPES studies [141]. Most of previous TPT studies assume a spatially uniform change of SOC with chemical doping. In reality, chemical doping inevitably introduces spatial inhomogeneity (e.g., SOC), so TPT might not happen in a spatially uniform manner. To illustrate this, we performed systematic nanoscale spectroscopic mapping across the TPT.

**Figure 4.7:** (a) VBM (blue), CBM (yellow) and Dirac point (violet) vs. $x$. The size of Dirac point symbols represent the spectra weight at Dirac point. (b) Estimated band gap at various $x$ showing a gradual increase of average band gaps. $x_c$: the critical point of TPT.

### 4.4 Nanoscale inhomogeneity of topological surface states

Fig. 4.8 shows the spectroscopy mapping results on all the six samples across the TPT. Fig. 4.8(a-f) show the topographic images where STS data were collected. In defects distribute randomly in the crystals. The $dI/dV$ maps of in-gap states (presumably the TSS) at the same locations are shown in Fig. 4.8(g-l). The $dI/dV$ maps of $x \leq 6.1\%$ are taken at $E = E_D + 0.05$ eV to enhance the contrast. We observed similar $dI/dV$ inhomogeneity in samples with substantial In concentrations. Note that the spatial inhomogeneity is also clear visible at different energies, e.g.,
$E - 0.1 \, \text{eV} \, [\text{Fig. 4.9(a-f)}]$ or $E + 0.1 \, \text{eV} \, [\text{Fig. 4.9(g-l)}]$. This indicates that such $dI/dV$ inhomogeneity is not limited to a small energy range. Instead, it is pronounced over the entire band gap. These results suggest non-uniform distributions of TSS in In-doped Bi$_2$Se$_3$. For $x > x_c$, the energy of the in-gap states (likely residue TSS) is marked by the arrow in Fig. 4.3(b). Clearly, the TSS is spatially inhomogeneous at nanometer scale.

Figure 4.8: (a-f) Topographic images of various $x$. Scale bars are 5 nm. (g-l) $dI/dV$ maps in the same area of (a-f). When $x \leq x_C$, $E = E_D + 0.05 \, \text{eV}$; for $x > x_C$, $E$ corresponds to residual TSS inside the gap, as marked in Fig. 4.3(b). Red (green) arrows mark typical TSS-weak (intense) regions. (m-r) average $dI/dV$ spectra of selective regions: Red (green) is from TSS-weak (intense) area.

In order to quantitatively characterize the difference between the area with low $dI/dV$ intensity and that with high $dI/dV$ intensity, we need to first unambiguously define the TSS-weak and TSS-intense area. Herein, we define them based on the spectral weight of $dI/dV(r)$ in the gap. The thresholds of defining these two area are chosen so that each of the two types of regions makes up 5% of the whole area. They can be found in Fig. 4.10(a). E.g., Fig. 4.10(b) plots the histogram of $dI/dV$ map of the sample of $x = 6.1\%$. The thresholds seperating the 5% area of the
Figure 4.9: $dI/dV$ maps in the same area as Fig. 4.8(g-l) at different energies: (a-f) $E - 0.1\text{ eV}$, (g-l) $E + 0.1\text{ eV}$. $E$ is the energy of $dI/dV$ maps in Fig. 4.8(g-l).

The lowest $dI/dV(r)$ and that of the highest $dI/dV(r)$ can be easily computed from the histogram: $t_1 = 0.010\text{ nS}$, $t_2 = 0.117\text{ nS}$. They are then applied to define the two types of regions: TSS-weak if $dI/dV(r) < t_1$; TSS-intense if $dI/dV(r) > t_2$. The same criterion is applied to all other $x$.

With the well-defined the TSS-weak area and the TSS-intense area, the average $dI/dV$ spectra in the two regions are shown in Fig. 4.8(m-r). In the TSS-intense area, the in-gap LDOS persists even when $x > x_C$. In contrast, the in-gap LDOS of TSS-weak area decreases rapidly to zero as $x$ rises. The linear dispersion of TSS is visible only when $x < x_C$. Note that the dramatic difference of $dI/dV$ spectra in TSS-weak and TSS-intense area is robust in a sense that it does not depend on the choice of threshold. If the proportion area of interest is chosen to be larger, e.g. 15%, the dramatic difference of average $dI/dV$ spectra in two areas still persists, as shown in Fig. 4.11.
Figure 4.10: (a) Histogram of $dI/dV(r)$ at various $x$. The solid lines separate TSS-weak and TSS-intense area. (b) Histogram of $dI/dV(r)$ of $x=6.1\%$ sample, demonstrating the definitions of TSS-weak and TSS-intense area.

4.5 Anticorrelation between the spectral weight of the topological surface states and local In density

More interestingly, we found that the inhomogeneity of the TSS correlates with the spatial distribution of In defects. Clearly there are more In defects in the TSS-weak area than in the TSS-intense area. To quantify the correlation, we computed the cross correlation ($X.Corr.$) between local In density $n(r)$ and the LDOS $dI/dV(r)$. Here we use $X.Corr.$ of the $x=4.8\%$ sample as an example. With atomic resolution, the locations of each In defect $R_{\text{In}}$ are identified in the topographic image shown in Fig. 4.12(a). Note that as $x \geq 9.0\%$, the uncertainty of In defect identification significantly vary, because In defects overlap with each other. The local In density $n(r,\zeta)$ is obtained by broadening the In position map with $\delta(r - R_{\text{In}})$ with a 2D Gaussian function $\left(1/\pi\zeta^2\right)e^{-r^2/\zeta^2}$, where $\zeta$ is the empirical correlation length. Since they are negatively correlated, the optimal correlation length $\zeta$ is chosen to minimize
Figure 4.11: Average $dI/dV$ spectra of TSS-weak and TSS-intense areas with different thresholds: 5% and 15%. The difference is robust as varying the threshold.

$X.Corr.$ of the two maps, $n(r)$ and $dI/dV(r)$ [Fig. 4.12(b-c)], which is defined by

$$X.Corr.(n, \Delta) = \frac{\int (n(r) - \bar{n})(dI/dV(r) - \bar{dI}/dV)dr}{\sqrt{\int (n(r) - \bar{n})^2dr \cdot \int (dI/dV(r) - \bar{dI}/dV)^2dr}} \hspace{1cm} (4.1)$$

As shown in Fig. 4.12(d), the minimum of $X.Corr.(n, \Delta)$ equal $-0.49$, indicating a strong anticorrelation between the local In density and spectral weight of TSS. At its minimum, the optimal correlation length of local In density map is $\zeta = 1.3 \text{ nm}$.

Figure 4.12: (a) Topographic image of 4.8% sample. (b) Local In density map $n(r)$ with proper broadening length ($\zeta = 1.3 \text{ nm}$). (c) $dI/dV$ map $dI/dV(r)$ in the same field of view as (a). (d) Cross-correlation ($X.Corr.$) between $n(r)$ and $dI/dV(r)$ as a function of $\zeta$. The green crosses and black dots represent the locations of In defects in the second atomic layer.

The anticorrelation is indeed observed in all the samples. The density maps of In defects are computed for various $x$, as shown in Fig. 4.13(a-f). The minimum $X.Corr.$ and the corresponding $\zeta$ as functions of $x$ are plotted in Fig. 4.13(g). The $X.Corr.$ is less than $-0.3$, and the average optimal correlation length $\zeta$ is $\sim 1.06 \text{ nm}$, which is consistent the decay length of the TSS ($\sim 0.94 \text{ nm}$).
The analysis above well establishes the fact that the TSS anti-correlates with the local In density $n(r)$ (counting only those in second layer) as shown by the negative cross correlation coefficients ($X.Corr.$) in Fig. 4.13(g). Note that it is practically impossible to count In defects at deeper layers. The observed anti-correlations indicate that In defects are very effective “suppressor” of topological band inversion [151]. Thus, it is imperative to reveal the impact of individual In defects on local topological properties.

### 4.6 Topological surface state suppression by individual In and In dimers

Fig. 4.14(a) shows the typical topographic image of a single In defect and an In dimer with nearest neighboring In defects on the 0.2% sample. Their configurations are illustrated in the schematic in Fig. 4.14(c). Fig. 4.14(b) shows a $dI/dV$ map measured at $E_D$ in the same area. Evidently the much lower spectro-weight on top of the In sites demonstrates that the TSS are strongly “suppressed” by In defects. This is further illustrated by the 2D spectral map (bias vs. displacement) of a $dI/dV$
Figure 4.14: (a) Topographic image of a single In and an In dimer on the second layer. Inset: simulated STM image of In defect by DFT. (b) STS map at $E_D$ in the same area as (a). (c) The top view of atomic structure of the top 2 atomic layers: Se (green), Bi (blue) and In (red). (d,e) $dI/dV$ intensity plots along the lines across single In (red) and In Dimer (blue). Tunneling conditions: $-0.6$ V, 0.5 nA. (f) Suppression of TSS at $E_D$ by In defects: blue, $dI/dV$ line profile across a In dimer; red, $dI/dV$ line profile across a single In defect; green: calculated $dI/dV$ of a single In defect. (g) Normalized Gaussian fitted of the $dI/dV$ spectra in (f): blue for In dimer; red for single In defects; purple for simulated overlapping of $dI/dV$ suppression by two single In defects.

The $dI/dV$ line profile across the center of a single In defect (red arrow in Fig. 4.14(b)) shown in Fig. 4.14(d). In addition, there is a slight increase of local band gap on the In defect, illustrated by the band edges (dash lines). The $dI/dV$ line profile at $E_D$ (red curves in Fig. 4.14(f)) shows a bell-shape suppression ($\sim 68\%$) with the full width half maximum (FWHM) $\xi \approx 1.17 \pm 0.03$ nm, indicating the influence range of single In defects extends to approximately $3a$ ($a \approx 0.41$ nm is the in-plane lattice constant). Interestingly, the FWHM $\xi$ is comparable with the decay length of TSS, $\xi_S = \frac{hv_F}{\Delta} \approx 0.94$ nm, where $v_F \approx 5 \times 10^5$ m/s is the Fermi velocity of Dirac surface.
states and $\Delta \approx 0.35 \text{eV}$ is the band gap [29]. The significant suppression of TSS indicates that a single In defect can be approximated as a point $\text{NI}$ embedded in the TI matrix.

![Top View](image)

Figure 4.15: Top view of atomic structure of the top 2 atomic layers of $(\text{Bi}_{1-x}\text{In}_x)_2\text{Se}_3$ with various types of In dimers on Bi layer.

More interestingly, the neighboring of In defects significantly enhances the suppression of local topological band inversion. Fig. 4.14(e) displays the 2D spectral map of $dI/dV$ spectra taken along the line across an In dimer [the blue arrow in Fig. 4.14(b)]. In addition to the further enhancement of local band gap, the suppression of TSS on In dimer is much stronger than that on single In defect, and is even stronger than a simple superposition of the suppression from two independent In defects. As shown in Fig. 4.14(g), the simple overlapping of two single In defects suppress the spectro-weight to 50%, while the observed spectro-weight of In dimer is reduced to $\sim 36\%$.

In addition to the In dimer of two nearest In defects, we also systematically studied In dimers of different separations between In defects. Fig. 4.15 illustrates the top view of atomic structure of $(\text{Bi}_{1-x}\text{In}_x)_2\text{Se}_3$ with various types of In dimers. The In dimer displayed in Fig. 4.14 is denoted by $D_1$ as the two In defects separate by one lattice constant. Similarly, the In dimers with separating distances of twice and three times of lattice constant are denoted by $D_{II}$ and $D_{III}$.

Fig. 4.16(e)-(h) display the effects of $D_{II}$. Clearly the the suppression of TSS by
Figure 4.16: Spectroscopic images of three different types of In dimers: (a-d) D_I; (e-h) D_II; (i-l) D_III. (a)(e)(i) Topographic images. (b)(f)(j) $dI/dV$ map (at $E_D$) obtained simultaneously with (a)(e)(i). (c)(g)(k) $dI/dV$ line profiles through the centers of In dimers (blue) and single In (red). (d)(h)(l) Normalized Gaussian fitted $dI/dV$ line profiles: blue for In dimer; red for single In defects; purple for the overlapping of $dI/dV$ suppression by two independent single In defects at the nearest neighboring sites.

The actual In dimer D_II (blue curve) is more effective than that of the simple overlapping of two independent In defects (violet). The result of In dimer D_III shown in Fig. 4.16(i)-(l) is even more surprising. Despite that the two In defects are well separated by $3a$, the interaction between them is still strong enough, as shown in Fig. 4.16(k). It is consistent with the influence range $\xi$ of single In defects. In a nutshell, the In dimers are more effective on locally suppressing the nontrivial topology than individual In defects.

DFT calculations were carried out to corroborate STM observation. The inset
of Fig. 4.14(a) shows a simulated STM image of single In defect, in good agreement with STM results. Furthermore, the simulated LDOS of TSS near In defects shows a similar suppression (green curve in Fig. 4.14(f)), which is also in good agreement with experimental results. Because the TSS are protected by the band topology (the surface-bulk correspondence), they cannot be “annihilated” without changing the band topology [5]. Thus, the local suppression of TSS spectro-weight likely comes from an effective increase of the tunneling barrier width. Because In defects convert nano-regions around them to NI, the interface between TI and NI (vacuum) is shifted slightly into the bulk, effectively increasing the tunneling barrier width and thus reducing the tunneling spectro-weight of TSS.

4.7 Inhomogeneity of local band gaps

The observation of enhanced band gap Δ on In defects suggest a positive correlation between local In density and local band gap Δ(r) (extracted from spectroscopy maps using the method mentioned in Section. 4.3.3). The curving fitting criterion given in Section. 4.3.3 can also be applied to individual single-point spectra in the $dI/dV$ grid maps, generating real-space maps of the CBM, the VBM as well as the local band gap Δ(r). The local band gap maps of various x are shown in Fig. 4.17(a-f). The means of these quantities, along with the results obtained in Sec. 4.3, are plotted together. The values of band edges [Fig. 4.17(g)] and band gaps [Fig. 4.17(h)] estimated by these two methods show very good consistency, indicating the robustness of our band edges and band gap analysis. Similar to the TSS, Δ(r) is also spatially inhomogeneous on the nanometer scale.

Fig. 4.18(a) shows the x dependence of average band gap $\langle Δ \rangle$ of selected regions. Δ(r) in the TSS-weak area (red arrows) is larger than that in the TSS-intense area (green arrows). $\langle Δ \rangle$ of TSS-weak regions increases rapidly while that of TSS-intense area changes little. Thus, the rise of $\langle Δ \rangle$ of the whole area (black curve) is mainly due
to the increasing areal fraction of TSS-weak regions. Furthermore, $\Delta(r)$ is correlated with local In density $n(r)$, as shown by the positive cross correlation coefficients ($X.Corr.$) in Fig. 4.18(b).

Figure 4.17: (a)-(f) Band gap maps of various $x$. (g) Estimated band edges. (h) Estimated band gap. Red curves are from linear curving fitting on average $\frac{dI}{dV}$ spectra; blue curves are the means of VBM, CBM and local band gap maps.

Figure 4.18: (a) Average band gaps of the whole (black), TSS-intense (green) and TSS-weak area (red) as functions of $x$. (b) $x$ dependence of the cross correlation coefficients between local In density $n(r)$ and band gap $\Delta(r)$. 

4.8 Discussion: Nanoscale mixture induced by strong local disorders

The observed nanoscale electronic inhomogeneity of TSS and band gap in In doped Bi$_2$Se$_3$ may be understood by a scenario illustrated in Fig. 4.19. In defects act as local topological-state “suppressors”, converting nano-regions around them to NI. For In defects near the surface, the normal nano-regions (NNR) push the TSS slightly into the bulk, as illustrated in the left panel in Fig. 4.19, so that the tunneling spectral weight of TSS is suppressed in surface-sensitive measurements [141]. As $x$ increases but $< x_c$, more regions with higher local In density form NNRs with larger band gaps in the matrix of topological regions which remain topological. For $x > x_c$, the topological regions form nano-size bubbles, denoted as topological nano-regions (TNRs) while the normal regions form the matrix. So the material is effectively a normal insulator (the right panel in Fig. 4.19). This phenomenological scenario qualitatively explains the nanoscale electronic inhomogeneity observed in our STM measurements. Further studies by other experimental techniques may help to better understand the unconventional TPT in In doped Bi$_2$Se$_3$.

It is worth noting that this scenario does not contradict the band-closure scenario of TPT, which assumes spatially uniform SOC so the band gap must close at $x_c$. In other words, the assumption of spatially uniform SOC is invalid for (Bi$_{1-x}$In$_x$)$_2$Se$_3$. In this system, the average band structure evolution across the TPT can be qualitatively illustrated by Fig. 4.20. Prior DFT studies suggest that In 5$s$ orbitals are very effective on suppressing SOC, thus In defects can revert the band inversion locally [151]. Therefore, In doping would inevitably introduce spatial SOC disorders, likely resulting in a mixture of TNRs and NNRs, a proliferation of TSS inside the bulk crystal, and a gradual increase of average band gap across the TPT [141]. The proliferation of TSS inside the bulk crystal is also consistent with the large enhancement of optical absorption around $x_c$ [140]. Finally the inhomogeneous TPT scenario
present here is different from the theoretical proposal of bypassing band gap closure via symmetry broken states [152].

Figure 4.19: Cartoon of the TPT due to nanoscale electronic inhomogeneity. The top and bottom are the boundaries of TI and vacuum. Left: In-dilute; Middle: underdoped, where topological regions dominate; Right: over-doped, where normal regions dominate.

Figure 4.20: Schematic scenario of evolution of band structure across the transition in $(\text{Bi}_{1-x}\text{In}_x)_2\text{Se}_3$. Yellow and blue bands represent conduction band and valence band. The color of surface state becomes lighter and lighter, indicating its strength gets weaker and weaker. And the overall band gap does not close across the whole topological transition.
4.9 Conclusion

To conclude this chapter, our results provide compelling microscopic evidence of an inhomogeneous TPT in (Bi$_{1-x}$In$_x$)$_2$Se$_3$, which is driven by nanoscale mixture of NNRs and TNRs, whose properties are summarized in Table 4.2. As shown by our systematic STM and STS studies, the inhomogeneity of both TSS and local band gap originates from very effective suppression of local SOC (and band topology) by In defects, resulting in local NNRs. Our results demonstrate that strong disorders can play a significant role in the TPT, which is difficult to capture in spatially average measurements. The direct observation of nanoscale inhomogeneous TPT will motivate further studies on the impact of SOC disorders in the topological materials and the associated quantum phase transitions.

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<th>Table 4.2: Properties of NNR and TNR</th>
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<td>Topological nano-regions</td>
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<td>TSS-intense area</td>
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<td>Smaller $\Delta(r)$</td>
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<td>Lower Indium density</td>
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Chapter 5

Electronic Fingerprints of Magnetic Dopants Cr and V in Topological Insulator (Bi,Sb)$_2$Te$_3$

This chapter is based on the work published in Zhang, Wenhan et al. *Phys. Rev. B* 98, 115165(2018) (Ref. [153]).

5.1 Motivation

Quantum anomalous Hall (QAH) state offers a promising platform to develop novel low energy-consuming electronic and spintronic devices and hence attracts a wide research interest in condensed matter physics. It is characterized by the spin-polarized dissipationless chiral edge states, which is a result of the topologically nontrivial band structures with the broken TRS [40]. The TRS can be broken by introducing FM order, via either the magnetic doping [40] or the magnetic proximity effect in TI/FM heterostructures [154]. To date, the chromium(Cr)- and vanadium(V)-doped (Bi,Sb)$_2$Te$_3$ are the only two systems that possess the QAH state [41, 42]. However, the full quantization in both systems requires extremely low temperature (T< 100 mK). Recently, Ou et al. achieved a significant increase of the characteristic QAH temperature in Cr/V co-doped (Bi,Sb)$_2$Te$_3$ films [43], where the critical temperature enhancement has been attributed to the improvement of the FM order [41, 42, 44, 45, 155, 46].

FM order has been reported in TIs doped with a number of 3d transition metal elements, e.g. Cr [156, 157, 158], V [159, 160, 161] and Mn [162, 163]. However, there is no consensus on the mechanism of the FM ordering in magnetically doped TIs. The
carrier-mediated exchange interaction (i.e. Ruderman-Kittel-Kasuya-Yosida interaction) has been predicted to be responsible for FM order especially in the presence of free bulk carriers in TIs [159, 164], similar to the case in conventional diluted magnetic semiconductors [165, 166, 167, 168]. In addition, a carrier-independent exchange interaction known as van Vleck mechanism was also proposed in magnetically doped TIs, which is the basis for the realization of QAH state [43, 40]. The van Vleck mechanism is independent of the spatial distribution of magnetic dopants. More recently, first-principles calculation studies suggest a new mechanism of carrier-independent exchange interaction in magnetically doped TIs [169, 170]. In this new mechanism, the $3d$ orbitals of magnetic dopants hybridize with the surrounding $p$-bonding network, resulting in a net spin density localized around magnetic dopants. Thus, the overlap of the hybridized states mediates the exchange coupling between magnetic dopants. Therefore, it is imperative to visualize the spatial distribution of these hybridized $3d$ states of magnetic dopants and to study the underlying exchange mechanism. Scanning tunneling microscopy/spectroscopy (STM/STS) is a powerful technique to image local electronic states with atomic resolution. So far, there are a few of STM studies on Cr- and V doped TIs [171, 172, 173, 174], only two of which are about the spatial distribution of the magnetic defect states [175, 176]. The comparison of the spatial distribution of the magnetic defect states between two parent systems for the QAH state (i.e. Cr- and V- doped Sb$_2$Te$_3$) is still lacking. Such a study will also facilitate the understanding of the enhancement of QAHE critical temperature in Cr/V co-doped (Bi,Sb)$_2$Te$_3$ [43, 177].

In this project, we performed systematic STM/STS studies on local electronic defect states of V and Cr dopants in Sb$_2$Te$_3$. The results are compared with first principles calculations done by our collaborators Prof. Shengbai Zhang’s group at RPI. Our work shows that the defect states of Cr are well above the CBM, while the defect states of V are located near the VBM, consistent with the DFT calculations. Our results demonstrate that the defect states of Cr and V dopants can serve as
electronic fingerprints to distinguish them in TIs. This study will pave the way to investigate the mechanism of enhanced FM order in Cr/V co-doped TIs and singling out materials candidates for the high-temperature QAH state. To avoid confusion, V represents vanadium in this chapter.

Figure 5.1: (a-c) Large-area topographic images for various defects, labeled from I to V. (d) High-resolution topographic images for defects I to V. (e-f) Top The dashed frame is the surface unit cell. (g) Calculated intrinsic defect formation energy under various growth conditions: the Te-rich condition corresponds to $\mu_{\text{Te}}$ set to that of bulk Te, whereas the Sb-rich condition corresponds to $\mu_{\text{Sb}}$ set to that of bulk Sb, with the constraint that $2\mu_{\text{Sb}} + 3\mu_{\text{Te}}$ equals the total energy of bulk Sb$_2$Te$_3$. Figures are adapted from Ref. [107].

5.2 Native Defects in Sb$_2$Te$_3$

Native defects widely exist in TIs. Experimentally, this often results in the situation in which the Fermi energy falls in the conduction band or valence band and thus the bulk is not fully gaped any more, which hinders intrinsic topological phenomena in the materials. To this end, it is of great interest and significance to control the defects so that the Fermi energy is brought to as high as the Dirac point on the surface. In addition, to differentiate the magnetic dopants Cr and V from the
native defects in the TI matrix, the identification and characterization is necessary for native defects. In 2012, Jiang et al. reported their work on tuning native defects in high-quality Sb$_2$Te$_3$ films grown by the molecular beam epitaxy (MBE) under different growth conditions [107]. They identified several native defects (Sb vacancy, Te$_{Sb}$ and Sb$_{Te}$), as shown in Fig. 5.1. The defects responsible for the natural p-type conductivity of Sb$_2$Te$_3$ are Sb vacancy and Sb$_{Te}$ in the strong Te-rich condition and the less Te-rich condition respectively. This could be explained by the first-principle calculation that they have the lowest formation energy in each condition, as shown in Fig. 5.1(g).

In Sb$_2$Te$_3$ single crystal samples, we found that the dominant native defect is Sb vacancies and a minor species is Sb$_{Te}$ antisite. Fig. 5.2 shows the topographic images on the pristine Sb$_2$Te$_3$ crystal. The defect shapes are consistent with the results in the thin film samples [107]. The concentrations of Sb vacancy and Sb$_{Te}$ antisite are $2.5 \times 10^{19}$ cm$^{-3}$ and $2.5 \times 10^{18}$ cm$^{-3}$ respectively. The crystal is on the Te-rich side.

![Topographic images of pristine Sb$_2$Te$_3$ crystal: (a) +1 V, 0.1 nA; (b) −0.1 V, 0.1 nA. The dominant defects are Sb vacancy and Sb$_{Te}$ antisite.](image-url)
5.3 Experimental methods

The V-doped and Cr-doped Sb$_2$Te$_3$ single crystals were grown with modified Bridgman methods by our collaborators Yew-San Hor’s group at Missouri University of Science and Technology. The stoichiometric mixtures of Sb (99.999%), Te (99.999%) and V (99.7%) or Cr (99.99%) with various nominal $x$ values were heated up to 950 °C at the rate of 1 °C/min in evacuated quartz tubes. The melts were maintained at the temperature for two days. Then they were cooled to 550 °C at the rate of 0.1 °C/min. The crystalline ingots were then quenched in cold water after a day of the 550 °C annealing.

The magnetically-doped (Bi,Sb)$_2$Te$_3$ films were grown by custom-built ultrahigh vacuum MBE systems. They were provided by Cui-Zu Chang’s group at MIT and Ke He’s group at Tsinghua. 10 nm Te was deposited on the top as a capping layer for ex-situ STM measurements. The Te capping layer was removed by sputtering and annealing the samples before STM measurements, as described in Chapter. 2.3.4.

5.4 Identification of magnetic defects in topographic images

Figs. 5.3(a-b) show representative topographic images of cleaved surfaces of V- and Cr-doped Sb$_2$Te$_3$ crystals. No interstitial V or Cr atoms were observed. All the V and Cr dopants occupy Sb sites, forming V$_{Sb}$ and Cr$_{Sb}$ defects at 2B or 4A sites (boxed in Figs. 5.3(a-b)) in the topmost quintuple layer (QL) as illustrated in Fig. 5.3(c). With sub-unit cell resolution, these magnetic defects at different depths can be unambiguously identified. The color images in Fig. 5.3(d) show the individual Cr and V defects. The magnetic defects at 2B sites are characterized by small dark triangles, while those at 4A sites are characterized by larger triangles with depressed corners and centers. The defects at 2B and 4A sites are crystallographically equivalent in the bulk, and thus the different appearances result from their different depths from the surface. Another type of prominent defects observed in both V- and Cr- doped
Sb$_2$Te$_3$ is the native Sb$_{Te}$ antisite, which has been demonstrated in Fig. 5.3(g). The dominant native defect Sb vacancy emerging in pristine Sb$_2$Te$_3$ become rare in the doped materials due to the excess cations. The Sb$_{Te}$ antisites at 3C site are not observed, probably because of a higher formation energy.

Figure 5.3: Topographic image of (a) V-doped Sb$_2$Te$_3$ and (b) Cr-doped Sb$_2$Te$_3$ (Tunneling condition: $-1$ V, 0.5 nA). Black squares mark V$_{Sb}$ or Cr$_{Sb}$ defects at 2B or 4A sites. Blue circles mark Sb$_{Te}$ defects at 1A and 5B sites. (c) Definition of atomic sites in the crystal structure of Sb$_2$Te$_3$. (d) STM images of individual magnetic defects. Colored images show experimental results; grey-scale images show the corresponding DFT simulations. (e) Crystal field splitting of 3$d$ electrons of V and Cr. (f) Zoom-in images of native defects Sb$_{Te}$ antisite at 1B and 5A sites.

The grey-scale images in Fig. 5.3(d) are the DFT simulated STM images of V and Cr at 2B and 4A sites. The excellent agreement between theory and experimental results further substantiates the identification of the magnetic defects. By counting V and Cr defects within the topmost QL, their concentrations can be quantitatively estimated: V(Cr) takes up 0.25%(0.4%) of each Sb layer. Because V and Cr dopants appear almost identical in topography at the typical sample bias (e.g., $-1$ V), it would be difficult to distinguish them in the Cr/V co-doped QAH films. Therefore, it
Figure 5.4: Bias-dependent topographic images of V and Cr defects. The six rows show different types of defects: \( V_I \) at 2B and 4A sites, \( V_{II} \) at 2B and 4A sites, Cr at 2B and at 4A sites, respectively. The sample bias varies from \(-1.0\) V to \(+1.0\) V.

is crucial to establish reliable criteria for differentiating V and Cr dopants. To address this issue, we perform bias-dependent topography measurements of the two materials. Fig. 5.4 shows the comparison of STM images of individual V and Cr defects at different sample biases. Interestingly, Cr(2B) appears as a triangular depression. It does not change much except at \( V = +0.6\) V, where its apparent shape rotates 180°. In contrast, we observed two types of V defects with different appearances. They are denoted as \( V_I \) and \( V_{II} \), respectively. Note that both of them occupy 2B or 4A sites, i.e., substituting Sb atoms. At high sample bias (\( |V| \geq 0.6\) V), their appearances are almost identical to that of Cr. On the other hand, the two types of V and Cr can be distinguished at low bias (\( |V| < 0.6\) V). \( V_I \) (2B) becomes a protrusion surrounded by 3 petals at \(-0.2\) V (the first row in Fig. 5.4), while \( V_{II} \) (2B) has a similar appearance.
at +0.2 V (the third row in Fig. 5.4). The changes of defect appearances of Cr and V at 4A sites are similar to those at 2B sites. The dramatic changes of the defect appearance, i.e., \( V_I \) at \(-0.2 \) V, \( V_{II} \) at +0.2 V and Cr at +0.6 V, suggest that V and Cr induce strong modulations in the local density of states (LDOS) in \( \text{Sb}_2\text{Te}_3 \) at different energies. Therefore, we performed spectroscopic mapping (\( dI/dV \)) of V- and Cr-doped \((\text{Bi},\text{Sb})_2\text{Te}_3\) to reveal the electronic and spatial distributions of defect states of V and Cr.

### 5.5 Electronic defect states of vanadium

Fig. 5.5(a) shows the average \( dI/dV \) spectra measured in selected regions of V-doped \( \text{Sb}_2\text{Te}_3 \). The blue spectrum was measured in defect-free areas. The steep increases in the \( dI/dV \) spectrum below \( E_F \) and above \( E_F + 0.3 \) V indicate the VBM and the CBM. The inset shows a V-shaped \( dI/dV \) spectrum due to the linear dispersion of the topological surface states. The minimum indicates that the Dirac point \( (E_D) \) is at 0.12 eV above \( E_F \), in agreement with previous studies [175, 107]. Interestingly consistent with the topographic images shown in Fig. 5.4, the two types of V have different \( dI/dV \) spectra. \( V_I \) has two peaks associated with the defect states: one at \( E_D - 0.20 \) eV, below the VBM; the other at \( E_D + 0.05 \) eV, inside the band gap. As for \( V_{II} \), a pronounced \( dI/dV \) peak is located at \( E_D - 0.07 \) eV, which is also in the band gap. The different defect states of the two types of V are the electronic origin of the dramatic change of their topographic appearances at a low sample bias.

The spatial distributions of the defect states of both \( V_I \) and \( V_{II} \) at 2B and 4A sites were visualized by spectroscopic imaging. Figs.5.5(d-f) show the \( dI/dV \) maps taken at \( E_D - 0.20 \) eV and \( E_D + 0.05 \) eV, where the defect states of \( V_I \) emerge. The defect states of \( V_I(2B) \) at \( E_D - 0.20 \) eV show a clover-like shape with three petals extending over \( \sim 2.1 \) nm. The in-gap defect states of \( V_I(2B) \) are clearly visible at \( E_D + 0.05 \) eV, which are spatially more extended \( (\sim 3.2 \) nm). On the other hand, Fig. 5.5(e) show
Figure 5.5: Electronic defect states of V. (a) Average $dI/dV$ spectra in selective regions of V-doped Sb$_2$Te$_3$: green (red) on V$_I$ (V$_{II}$); blue in the defect-free area ($-0.5$ V, 1 nA). Inset: $dI/dV$ spectra of the surface states measured in defect-free areas. (b) DFT calculated band structure of V$_{0.03}$Sb$_{0.97}$Te$_3$ and partial DOS, as well as the $dI/dV$ difference between V sites with defect-free areas. The arrows indicate the energies of the defect states. (c) Topographic image of V-doped Sb$_2$Te$_3$ ($-1.0$ V, 0.5 nA), which contains both V$_I$ and V$_{II}$ at both 2B and 4A sites. (d-f) $dI/dV$ maps taken in the same area as (c) at $E_D-0.2$ eV, $E_D-0.07$ eV and $E_D+0.05$ eV, respectively. The defect states of V$_I$ are pronounced in (d) and (f), while those of V$_{II}$ in (e). (g) Zoom-in $dI/dV$ images of in-gap defect states of V$_{II}$ and the DFT simulations.

that the defect states of V$_{II}(2B)$ stand out at $E_D-0.07$ eV, corresponding to the in-gap peak in the $dI/dV$ spectrum. As for the V dopants occupying 4A sites, the defect states of V$_{II}(4A)$ at $E_D-0.20$ eV are invisible. They may be smeared out by the bulk states of Sb$_2$Te$_3$ since V$_{II}(4A)$ is deeper from the cleaved surface than V$_{II}(2B)$. The intensity of in-gap defect states of V$_{II}(4A)$ at $E_D+0.05$ eV and V$_I(4A)$ at $E_D-0.07$ eV is weaker and more extended ($\sim4.1$ nm) than V(2B). The appearances of the in-gap defect states of V$_I$ and V$_{II}$ are very similar, suggesting a similar electronic origin.

The crystal field in the octahedral environment of V dopants splits the d-levels into triplet $t_{2g}$ and doublet $e_g$ states as shown in Fig. 5.3(c). The majority spin channel
of the low lying $t_{2g}$ states is occupied with 2 electrons leading to magnetic moments of $2\mu_B$ per vanadium ion. The band structure of $V_{0.03}\text{Sb}_{1.97}\text{Te}_3$ calculated via DFT is shown in Fig. 5.5(b). The calculated partial density of states (pDOS) of V shows a peak at $E_D$, which is attributed to the impurity bands inside the band gap mainly coming from V $t_{2g}$ orbitals. This feature is in better agreement with $V_{II}$ defect states. Consistently, the spatial distribution of defect states in the DFT simulation [grey-scale images in Fig. 5.3(g)] resembles the clover-leaf shape as observed in experiment [color images in Fig. 5.3(g)].

Although there is a clear difference between the defect states of $V_I$ and $V_{II}$, its origin remains unclear. One possible scenario is that a slight Jahn-Teller distortion occurs around $V_I$ dopants and further splits their $t_{2g}$ orbitals. However, our STM is not able to resolve any local distortion around $V_I$ dopants. Alternatively, it may originate from distinct electronic environments induced by other charge defects. We did not find a clear correlation between V dopants and other charge defects (e.g. $Sb_{Te}$) either. The physical origin of $V_I$ reamians a mystery and its impact on exchange coupling will be investigated in future studies. If the concentration of V dopants is sufficiently high, these local defect states would overlap and likely form impurity bands. Recent ARPES studies suggest that V doping causes the VBM of V-doped $(\text{Bi,Sb})_2\text{Te}_3$ to lie higher in energy than the Dirac point [164]. In light of our observations of pronounced local defect states near the Dirac point, the upshift of the VBM may originate from the formation of the impurity band from V defect states.

### 5.6 Electronic defect states of chromium

Fig. 5.6(a) shows the $dI/dV$ spectra taken on Cr defect sites (red) and defect-free areas (blue). Cr does not contribute defect states inside the band gap. Surprisingly, a peak in the $dI/dV$ spectrum of Cr defects emerges at $E_D + 0.48$ eV, which is well above the CBM. Fig. 5.6(c) shows a representative topographic image with atomic
resolution where individual Cr dopants at 2B and 4A sites were observed. Fig. 5.6(d) shows the spatial distribution of Cr defect states visualized with $dI/dV$ imaging at $E_D + 0.48$ eV. As far as we are aware of, these Cr defect states have not been reported in prior studies. To confirm the experimental observation, our collaborators calculated the band structure and the Cr pDOS in $\text{Cr}_{0.03}\text{Sb}_{1.97}\text{Te}_3$ via DFT. The results are shown in Fig. 5.6(b). The hybridized band with dominant $e_g$ orbitals of Cr is deep inside the conduction band, in good agreement with the experimental results. Furthermore, the calculated spatial distribution of Cr defect states [Fig. 5.6(e)] is consistent with experimental observation. The excellent agreement between theory and experiment provides compelling evidence that the observed Cr defect states are intrinsic.

Figure 5.6: Electronic defect states of Cr. (a) Average $dI/dV$ spectra in selective regions of Cr-doped $\text{Sb}_2\text{Te}_3$: red near Cr and blue in the defect-free area (+0.9 V, 1 nA). Inset: $dI/dV$ spectra of the surface states measured in defect-free areas. (b) DFT calculated band structure of $\text{Cr}_{0.03}\text{Sb}_{1.97}\text{Te}_3$ and the partial DOS of Cr, as well as the experimental $dI/dV$ difference between Cr sites with defect-free areas. (c) Topographic image of Cr-doped $\text{Sb}_2\text{Te}_3$ (−1.0 V, 0.5 nA), which contains Cr defects at both 2B and 4A sites. (d) $dI/dV$ map taken in the same area as (c) at $E_D + 0.48$ eV, showing the local defect states high above the CBM. (e) the DFT simulated spatial distribution of defect states of Cr.
5.7 Enhancement of defect states by neighboring magnetic dopants

Similar to the enhancement effect of Indium in Bi$_2$Se$_3$ demonstrated in Chapter 4, herein we also observed an enhancement of local defect states of Cr and V in Sb$_2$Te$_3$ caused by proximity of magnetic defects. We measured the $dI/dV$ grid maps in the areas where Cr-Cr dimers emerge with separations from $2a$ to $6a$, as shown in Fig. 5.7(a-e). The corresponding $dI/dV$ maps at the energy of occurrence of the Cr defect state are shown in Fig. 5.7(f-j). If the distance between two Cr defects is $\leq 3a$, the intensity of the defect state is higher than that of a single Cr defect [Fig. 5.8(a)]. The defect state in the overlapping area persists to as far as $d = 6a$, which is comparable to the characteristic length scale of the distribution of the defect states of a single Cr [Fig. 5.8(b-c)].

![Figure 5.7: Defect states of Cr dimers with various separations. (a-e) Topographic images of single Cr and Cr dimers at 2B sites with separations of $2a$ to $6a$. (f-j) $dI/dV$ maps in the same areas as (a-e) measured at $E_D + 0.48$ eV.](image)

The enhancement of defect states of V dimers is more significant. We measured V$_1$-V$_1$ dimers with separations of $3a$ and $5a$, as shown in Fig. 5.9(a) and (e), respectively. The $dI/dV$ maps [Fig. 5.9(b-d),(f-h)] presents the typical defect states taken at $-0.08$ eV, $-0.01$ eV and $0.25$ eV. A clear increase of intensity of defect states
Figure 5.8: (a) $dI/dV$ spectra between neighboring Cr defects of a dimer. Red arrows in Fig. 5.7 mark the locations where these $dI/dV$ spectra were taken. Compared with single Cr, there is an enhancement of defect state intensity in the Cr dimers if $d < 4a$.

(b) The different spectra between those shown in (a) and the $dI/dV$ spectrum in the defect-free area. (c) The $dI/dV$ intensity at the peak of defect states as a function of the distances between Cr atoms within a dimer.

occurs: At $-0.01$ eV, the $dI/dV$ spectrum of the 3a dimer shows a peak instead of a hump in that of single V defect; At 0.25 eV, the $dI/dV$ spectra of both the 3a and 5a dimer show an intensity much larger than that of single V defect[Fig. 5.9(h)]. V$_{II}$-V$_{II}$ dimers show an even stronger enhancement of defect states in the overlapping area. As shown in Fig. 5.10, the overlapping area of such a dimer with $d = 2a$ [Fig. 5.10(a)] presents a dramatic peak at $+0.1$ eV. The intensity of the peak of LDOS is as high as the bulk states near the VBM [Fig. 5.10(b)]. The corresponding $dI/dV$ maps at $-0.08$ eV and $+0.1$ eV are shown in Fig. 5.10(c-d).

Compared with chromium defects, vanadium defects in proximity present much more pronounced enhancement. One of the aforementioned possible mechanism of magnetic ordering suggests that the 3$d$ orbitals of magnetic dopants hybridize with the $p$-bonding network of TI matrix and that the overlap of the hybridized states mediates the exchange coupling. Thus the observed enhancement of defect states due to their proximity may greatly facilitate the exchange coupling. If this mechanism is dominant in establishing the magnetic ordering in the magnetic TIs materials, the larger enhancement of defect states of V over Cr may explain why the magnetic
properties of V-doped QAH materials is better than those of Cr-doped QAH materials [42].

Figure 5.9: Defect states of V₁ dimers. (a,e) Topographic images of the V₁ dimers at 2B sites with separations of 3a to 5a. (b-d) dI/dV maps in the same areas as (a) measured at −0.08 eV, −0.01 eV and 0.25 eV. (f-h) dI/dV maps in the same areas as (e) measured at −0.08 eV, −0.01 eV and +0.25 eV. (i) dI/dV spectra measured at the center of V₁ dimers.
Figure 5.10: Defect states of V$_{II}$ dimers. (a) Topographic images of the V$_{II}$ dimers at 2B sites with a separation of 2$a$. (b) $dI/dV$ spectra measured at the center of V$_{II}$ dimers. (c-d) $dI/dV$ maps in the same areas as (a) measured at −0.08 eV and +0.1 eV. A huge enhancement of $dI/dV$ intensity of the defect state is observed.

5.8 Identification of chromium and vanadium in (Bi,Sb)$_2$Te$_3$ thin films

We measured the V-doped (Bi,Sb)Te films grown by the MBE method. The samples were protected by amorphous Te layer, which was removed in the preparation chamber before STM measurements. The defect states we observed in the single crystals are indeed reproducible in the film sample. Fig. 5.11 shows the results taken on the film with the nominal stoichiometry of V$_{0.09}$Sb$_{1.91}$Te$_3$. The topographic images
measured at $-1.0$ eV and $-0.2$ eV [Fig. 5.11(a-b)] present consistent bias-dependent defect shapes of $V_I$ in the crystals. The zoom-in STM image in Fig. 5.11(c) were measured in the lower half area of Fig. 5.11(a). In the same area, the $dI/dV$ grid map was measured. The $dI/dV$ maps [Fig. 5.11(d-e)] and the $dI/dV$ spectra [Fig. 5.11(f)] show defect states that are consistent with $V_I$ defects. In addition, the enhancement of in-gap defect state in the overlapping region is demonstrated as well (green allow in Fig. 5.11(e) and green spectrum in Fig. 5.11(f)).

Figure 5.11: V-doped Sb$_2$Te$_3$ film. (a-b) Topographic images taken at $-1$ V and $-0.2$ V. The image size is $30$ nm $\times$ $30$ nm. (c) Zoom-in STM image with the atomic resolution where multiple V defects exist. (d-e) $dI/dV$ maps at $\pm 0.2$ eV shows the distribution of defect states. (f) $dI/dV$ spectrum taken in the defect-free area, on top of V and in the overlapping area of V-V defects. The defect states of V in the film is consistent with that of $V_{II}$ in the crystals.

To corroborate that the measured defect states of Cr and V serve as electronic fingerprints to differentiate them in the QAH material, we studied the film of $(V,\text{Cr})_y(\text{Sb, Bi})_{2-y}\text{Te}_3$ which has the same stoichiometry as those presenting the enhanced QAHE [43]. Fig. 5.12(a) shows a large-scale image of the sample. As demonstrated in Fig. 5.4, bias-dependent topographic images provides a convenient way to
differentiate Cr and V defects. The shape of Cr does not change much as the sample bias changes, i.e., from $-1\,\text{V}$ to $-0.2\,\text{V}$, while that of V changes dramatically. With this criterion, we first mark all the exotic defects in the topographic image taken at $-1\,\text{V}$ [E.g., Fig. 5.12(b)], where both V and Cr defects appear as triangular depressions. Then, we differentiate Cr and V defects in the topographic image taken at $-0.2\,\text{V}$. At this bias, Cr defects remain a triangular depression, while V defects appear as protrusions, as shown in Fig. 5.12(c). Following this procedure we successfully achieved the defect identification of Cr and V in a larger area, as shown in Fig. 5.12(d-f). We calibrated the defect density with the topographic images, which gives $y = 0.04$ and the ratio of Cr and V $\text{Cr} : \text{V} = 1 : 3$.

Figure 5.12: Topographic images of $(V,\text{Cr})_y(\text{Sb, Bi})_{2-y}\text{Te}_3$ thin films. (a) Large scale, tunneling condition: $-1\,\text{V}, 100\,\text{pA}$. (b-c) Atomically resolved images measured in the clean area shown in (a). The tunneling conditions of (b) and (c) are $-1\,\text{V}, 2.5\,\text{nA}$ and $-0.2\,\text{V}, 1\,\text{nA}$, respectively. (d-f) Topographic images of different area with a number of Cr and V defects resolved. The blue and red boxes mark the locations of V and Cr, respectively. The size of (d-f) is $50\,\text{nm} \times 50\,\text{nm}$. 
5.9 Conclusion

In summary, our spectroscopic imaging shows that the V defect states contribute finite LDOS in the band gap of TIs because of the partially filled $t_{2g}$ orbitals. In contrast, the Cr defect states are deep in the conduction bands. Both V and Cr defects show nontrivial spatial distributions of local electronic defect states, which is corroborated by the DFT calculations. The bias dependent study of defect shapes in topographic images provide a convenient criterion to differentiate Cr and V in the codoping samples. Our measurements on MBE-grown TI films demonstrate that these unique distributions of V and Cr defect states can indeed be used as electronic fingerprints to investigate the interaction between dopants in Cr/V co-doped TIs with higher temperature QAH state. Most importantly, systematic spectroscopic imaging studies of co-doped TIs may shed new light on the magnetic exchange mechanism and could lead to the QAH state realized at elevated temperatures for potential technological applications. There are still a number of interesting mysteries to be unraveled: 1. What is the origin of two types of V defects in crystals? 2. How does the enhancement of electronic defect state of neighboring defects associate with the magnetic coupling mechanism? 3. What is the electronic origin of enhancement of QAH temperature in V and Cr co-doped samples? Subsequent experimental and theoretical studies will address these questions.
Chapter 6
Quasiparticle Interference of Surface Fermi Arcs in the Type-II Topological Weyl Semimetal WTe$_2$

This chapter is based on the work published in Zhang, Wenhan et al. Phys. Rev. B 96, 165125(2017) (Ref. [178]).

6.1 Quasiparticle interference

In solid materials, the eigenstates of electrons are the Bloch wave functions due to the periodic potential. They are characterized by well-defined wave vector $k$ and energy $\varepsilon$. The energy-momentum dispersion $\varepsilon(k)$ can be measured with momentum resolved techniques, e.g., ARPES. In comparison, real-space image techniques such as STM cannot directly measure such dispersion. This is because the LDOS captured by STS at a certain location is associated with the eigenstates by

$$LDOS(E, r) \propto \sum_k |\psi_k(r)|^2 \delta(E - \varepsilon(k)),$$

(6.1)

and by substituting a Bloch wave function into the above equation, one can solve LDOS to be spatially uniform. However, imperfections such as step edges, defects or impurities will cause scattering between the eigenstates of different $k$. As illustrated in Fig. 6.1, due to the phase coherence, the incoming wave function $\psi(k_i)$ interferes with the outgoing wave function $\psi(k_f)$, forming an interference pattern with wave vector of $q = k_f - k_i$. The corresponding wavelength of the spatial LDOS modulation is $\lambda = 2\pi/q$. STM can observe such LDOS modulation as spatial modulation of differential conductance $dI/dV$ in the spectroscopic grid imaging, which is discussed
in Chapter 2. To reveal the periodic modulations from all the allowed scatterings, it is useful to compute the Fourier transform (FT) of the $dI/dV$ maps. In the momentum space ($q$-space), one can separate the coexisting modulations. They are manifested as bright spots in the FT of the $dI/dV$ maps. Each modulation emerges at the locations with high intensity in the FT of $dI/dV$ maps. By tracking the scattering $q$ at each energy $\varepsilon$, one can obtain the dispersion $\varepsilon(q)$ of the scattered electronic waves.

Figure 6.1: Illustration of elastic scattering of eigenstates by a point scattering center.

### 6.2 Motivation

TWS processes many interesting exotic properties, such as surface Fermi arcs [50, 55] and unconventional magneto-transport phenomena due to the chiral anomaly [56, 57, 58, 59, 60, 61, 62]. Among the interesting properties of TWSs, surface Fermi arc is a crucial property associated with the non-trivial topological nature of the bulk states. Therefore, visualizing such surface states, and proving their topological origin, is one of the major efforts in studies of TWS. Angle-resolved photoemission spectroscopy (ARPES) studies on both type-I (TaAs family) [64, 65, 66, 179] and type-II TWS (transition metal dichalcogenides) [180, 181, 182, 183, 184, 185] have provided evidence of surface states, but whether the appearance of these states in the
type-II TWS is a result of type-II Weyl points in the bulk remained unanswered. STM is a powerful technique to characterize the surface states of TWS via quasiparticle interference (QPI) from spectroscopy measurements [186, 187]. It can measure both the occupied and unoccupied states with excellent energy resolution, while ARPES accesses only occupied states normally. This motivated scanning tunneling spectroscopy (STS) on WTe$_2$ to visualize the QPI due to surface states.

STS measurments have been performed on several TWS materials, which include TaAs [188, 189, 190], NbP [191] and MoTe$_2$ [181]. However, despite several prior STM studies on WTe$_2$ [164, 192], the clear evidence of surface states of WTe$_2$ above $E_F$ is still absent. Due to coexistence of the electron and hole pockets with Weyl nodes near the Fermi energy, the bulk states also contribute significantly to the surface scattering, which complicates the identification of the surface states. Therefore, it is necessary to compare experimental QPI results with first principle calculations to differentiate QPI feature of surface states from that of bulk states.

In this work, we used STM/STS to directly visualize QPI patterns of surface states from two distinct surfaces of WTe$_2$ single crystals. For comparison, we also carried out density functional theory (DFT) calculations and obtained surface spectral weight maps as well as the corresponding spin-preserved joint density of state (JDOS) maps at various energies. The good agreement between DFT calculations and experiments confirms that the main QPI is from scattering between two surface Fermi arcs in the surface BZ. The solid evidence of surface states on WTe$_2$ will stimulate further investigation of topological nature of surface states in TWS materials.

### 6.3 Experimental and calculation methods

We studied the single crystal samples of WTe$_2$, which were grown via iodine vapor transport method by Prof. Sang-Wook Cheong’s group at Rutgers. Tungsten powder (99.9%) and tellurium powders (99.99%) were well-mixed and heated in an
evacuated silica tube at 700 °C for 2 days; the synthesized product was then ground and heated at 750 °C for 2 days. The final pellet was ground into fine powders. Appropriate amount of powders and iodine were sealed in an evacuated silica tube and put in a two-zone furnace with a temperature gradient of 50 °C between 850 °C and 800 °C for 1 week.

To differentiate two polar surfaces, one piece of WTe$_2$ single-crystal was cut into two halves and one of them was flipped upside down. Then both samples were carefully mounted on STM sample plates without changing their orientations. They were cleaved *in-situ* in ultra-high vacuum at room temperature, then were immediately transferred into cold STM head for measurements. Since WTe$_2$ single crystals are always in single polar domain state, the cleaved surfaces of the flipped crystal is presumably opposite to the other one. The $dI/dV$ grid mapping measurements were performed to probe the QPI of the surface states.

On the theoretical side, our collaborators Quansheng Wu and Alexey A. Soluyanov at Zürich performed electronic structure calculations using the DFT method. The spin-dependent JDOS maps were calculated as

$$J_s(q) = \frac{1}{2} \sum_{\mathbf{k}} \sum_{i=0,1,2,3} \rho_i(\mathbf{k}) \rho_i(\mathbf{k} + \mathbf{q}),$$  \hspace{1cm} (6.2)

where total spectral density $\rho_0(\mathbf{k}) = -\frac{1}{\pi} \text{Im}[\text{Tr} G_s(\mathbf{k}, \epsilon_0)]$, $G_s(\mathbf{k}, \epsilon_0)$ is the surface Green’s function at momentum $\mathbf{k}$ and energy $\epsilon_0$ relatively to $E - F$, and the spin density $\rho_i(\mathbf{k}) = -\frac{1}{\pi} \text{Im}[\text{Tr}[\sigma_i G_s(\mathbf{k}, \epsilon_0)]]$, $i = 1, 2, 3$ with $\sigma_{1,2,3}$ being the Pauli matrices of electron spin.
6.4 Topographic images and $dI/dV$ spectrum

Fig. 6.2(a) and (b) display the schematic bulk atomic structure and its Brillouin zone of WTe$_2$. Due to the lattice distortion, WTe$_2$ has orthorhombic unit cell with the space group $Pmn2_1$ [193, 67]. Correspondingly, the surface Te atoms distort and form chains along $a$ axis, as shown by large scale topography in Fig. 6.2(c). In the zoom-in topographic image [the left inset of Fig. 6.2(c)], two inequivalent Te atomic chains are visible. The one with higher apparent height has better atomic resolution. The lattice constants estimated by the Bragg peaks in the right inset of Fig. 6.2(c) are $a = 3.51$ Å and $b = 6.27$ Å, which are consistent with the previous reports [193, 164]. The orthorhombic lattice structure was repeatedly observed on multiple pieces of WTe$_2$ samples within our STM orthogonal uncertainty ($< 2^\circ$). There are a number of point defects emerging on the surface of the sample (white dots in Fig. 6.2(c)). The defect concentration is ideal for the QPI measurement. We measured the $dI/dV$ spectrum [Fig. 6.2(d)], which is proportional to the LDOS of the sample. It shows a semi-metallic behavior. The calculated total DOS of bulk WTe$_2$ [Fig. 6.2(e)] qualitatively agrees with the measurements.

6.5 Calculated spectral weight maps

Prior band structure calculations of WTe$_2$ [193] reveal that both the valence band and conduction band cross the Fermi level, forming electron and hole pockets. This has been confirmed by ARPES studies [194]. The calculations also predict that the Weyl points locate at around 50 meV above $E_F$ [67]. Fig. 6.3 (a) and (b) plot the calculated spectral weight maps of bulk and surface states at various energies by projecting electronic states to the surface Te layers.

The surface Fermi arcs are marked by the black dashed lines. The hole pockets locate closer to the $\Gamma$ point than the Fermi arcs. As the energy increases, they shrink and disappear. The electron pockets, on the other hand, locate farther from the $\Gamma$
Figure 6.2: (a) Crystal structure of WTe$_2$. (b) Schematics of bulk and surface Brillouin zones. (c) Large-scale topographic image of WTe$_2$. ($V_B = 1$ V, $I_T = 10$ pA) Left inset: Zoom-in topographic image ($V_B = 0.01$ V, $I_T = 2.4$ nA). Right inset: Fourier transform of the left inset image showing Bragg peaks corresponding to the atomic corrugation. (d) Average $dI/dV$ spectrum taken on WTe$_2$ surface. ($Bias = -1$ V, $I_T = 1$ nA) (e) Calculated total density of state.

point than the Fermi arcs. They grow larger at higher energy. In order to emphasize the surface states, projections from the bulk states have been removed. The spectral weigh maps of the surface states are display in Fig. 6.3 (c) and (d). Due to the broken inversion symmetry, the top and bottom surfaces of WTe$_2$ have inequivalent band structures. And this is confirmed by our calculated surface Fermi arcs on different surfaces. However, the dispersions of the surface Fermi arcs on these two surfaces are qualitatively the same. They are most visible from $E_F - 40$ meV up to $E_F + 60$ meV. As the energy increases, the arc-like surface states gradually moves toward Γ point (the BZ center). They completely disappear above $E_F + 60$ meV. It is in good agreement with constant energy contour results in ARPES experiments [183, 182, 184]. The surface Fermi arcs have non-trivial spin texture, which has been reported in Ref. [195]. The spin texture of the surface states at $E_F$ is illustrated in Fig. 6.4. This needs to be considered when calculating the JDOS, as addressed by Eq. 6.2.
6.6 Quasiparticle scattering around point defects

With the guidance of calculated spectral weight maps of surface states, we performed spectroscopic grid mapping on two distinct surfaces of WTe$_2$ to investigate energy-dependent QPI patterns. We locate a region on surface-1 with sufficient defect density, as shown in Fig. 6.5(a). The fast scan axis is chosen to be parallel with the atomic chain (a axis). The major defects appear as surface suppression, indicating they may be subsurface vacancies or anti-sites. Clear spatial scattering around defects was observed in the $dI/dV$ maps between $-100$ meV and $+100$ meV. Fig. 6.5(b) displays a representative $dI/dV$ map at $+40$ meV. Note that there are more scattering centers in the $dI/dV$ map [Fig. 6.5(b)] than the surface defects observed in the topographic image of Fig. 6.5(a). They are probably defects underneath the surface.
Te layer. Two different patterns are commonly observed in the $dI/dV$ maps at various energies: one is the $dI/dV$ modulations localized on top of the defect cites (white spots at the center of Fig. 6.5(e)); the other is the much weaker but extended standing waves around defects. Fig. 6.5(f) displays the line profiles taken on the topographic images [Fig. 6.5(c)(d)] and the $dI/dV$ map [Fig. 6.5(e)] across an isolated defect. The length scale of that localized $dI/dV$ modulation is $l \sim 5$ nm, the same as the defect size, indicating that it is a result of impurity potential or defect states. In contrast, the oscillating pattern spreads about 17 nm away from the defects with well defined spatial periodicity $\lambda \sim 1.1$ nm along a direction, suggesting that it is the QPI pattern. Thus, based on the different length scales, the QPI pattern is unambiguously separated with the $dI/dV$ modulations induced by the defect potential. The spectroscopic data of the other surface (not shown) present the same features.
Figure 6.5: (a) Topographic image where the $dI/dV$ grid mapping was performed. ($V_B = -1 \text{ V}, I_T = 100 \text{ pA}$) (b) The $dI/dV$ map at $E = E_F + 40 \text{ meV}$ in the same field of view as (a), showing quasiparticle scattering patterns around defects. (c) A zoom-in topographic image of an individual defect at $V_B = -1 \text{ V}$. (d) A topographic image at $V_B = -0.1 \text{ V}$ in the same field of view as (c). (e) A $dI/dV$ map at $E = E_F + 40 \text{ meV}$ in the same field of view as (c). (f) Line profiles of the topographic heights (red and orange) and $dI/dV$ signals (blue). The positions where they were taken are marked by arrows in (c)-(e). The purple curve is the $dI/dV$ line profile in defect-free area, as marked in (b).

6.7 Dispersion of QPI of the surface states

Fourier transforms (FTs) of the $dI/dV$ maps in Fig. 6.6(a)-(h) display the $q$ (scattering wave vector) maps of QPI in the surface BZ in the energy range from 0 up to $+60 \text{ meV}$. Several non-trivial features were observed: red and green arrows point to a sharp pattern evolving towards $\Gamma$ point as the energies increases, and the purple arrows mark a non-dispersive pattern that fades out gradually and disappears when $E > E_F + 40 \text{ meV}$. The FT intensity around $\Gamma$ point is very high, but no sharp features are observed there. The sharp pattern locates at $q_x \sim 0.55 \text{ Å}^{-1}$, equivalent to $\frac{2\pi}{\lambda}$, indicating its correspondence to the spatial LDOS modulation shown in Fig. 6.5(f). Its dispersive character is manifestly illustrated in Fig. 6.6(r). As for the $dI/dV$ modulation localized at defect centers, the corresponding $q$ value is about $0.13 \text{ Å}^{-1}$,
which is much closer to the Γ point than the observed QPI. To understand the origins of these features in the \( q \) maps, the surface JDOS maps were calculated.

\( \text{WTe}_2 \) is a non-magnetic type-II TWS. The time reversal symmetry prevents scatterings between the states with opposite spins. This has been confirmed by STM studies of other non-magnetic TWSs [188, 191, 181, 196]. Therefore, the spin-preserving JDOS calculations are necessary to compare to the FTs of the \( dI/dV \) maps. Fig. 6.6(i)-(p) show the images of spin-preserved JDOS of surface states at the same energies with Fig. 6.6(a)-(h). The X-shaped feature at Γ point mainly originates from the intra-arcs scattering of the Fermi arcs and the arc-like features on the left and right sides correspond to the inter-arc scattering. As the energy increases, the inter-arc scattering features marked by the blue and orange arrows gradually move towards Γ point. This trend is consistent with the evolving feature marked by red and green arrows in the FTs of the \( dI/dV \) maps in Fig. 6.6(a)-(h), suggesting that the red- and green-arrow pattern originates from the surface state scattering.

To quantitatively compare the experimental QPI maps and calculated JDOS maps, the dispersions of the sharp pattern in Fig. 6.6(a)-(h) are extracted and plotted together with the scattering vector obtained from DFT calculations, as shown in Fig. 6.6(s). Here \( q_1 \) and \( q_2 \) represent the scattering vectors connecting the heads and tails of the two Fermi arcs respectively, as illustrated by Fig. 6.6(q). With the presence of time reversal symmetry, the states at the apex of the two Fermi arcs \( (k_y = 0) \) must have opposite spins, meaning the surface state scattering \( q_1 \) is suppressed. Yet scattering vectors between \( q_1 \) and \( q_2 \) are allowed. The experimentally observed scattering vectors indeed fall in the range between \( q_1 \) and \( q_2 \) at various energies. The good agreement shows that the sharp feature captured in QPI patterns originates from scattering between surface states of Fermi arcs. In addition, the pattern marked by purple arrows in Fig. 6.6(a)-(h) does not associate with the surface state scattering. It may result from the scattering between bulk states. Within the experimental uncertainty, the two surfaces present essentially identical QPI features.
It is also consistent with our DFT calculation results, that the two surfaces have qualitatively the same electronic structure.

6.8 Discussion and summery

It is still under debate whether the observed surface states are topological or trivial [183, 182, 184]. On one hand, small changes of lattice structure may change the topological nature of the material [183]. On the other hand, even in the topological phase, the trivial and topological surface states coexist and are in close proximity in $k$-space, so it is very difficult to distinguish them experimentally. Furthermore, a recent work reported the Rashba spin splitting effect on WTe$_2$ surface [164], suggesting that the trivial surface states may also be spin-polarized. This makes it more difficult to identify the topological surface states unambiguously.

In this work, we combined STM/STS measurements and first principle calculations to resolve the surface states on the (001) surface of WTe$_2$. The QPI patterns indicate the scattering of dispersive surface states. The calculated spin-dependent J-DOS maps further confirm the existence of surface states on WTe$_2$. Our work provides evidence of the surface states on type-II TWS WTe$_2$ and may inspire the subsequent research to figure out the topology of such surface states in semi-metallic TWSs. This works demonstrated that with the existence of reasonable amount of the point defects in the materials, quasiparticle interference is a powerful technique to reveal the energy-momentum dispersion of surface states, which are well defined in the 2D surface Brillouin zone.
Figure 6.6: (a)-(d) Fourier transforms of $dI/dV$ maps taken on surface 1 from $E_F$ to $E_F + 60$ meV. The red arrows point to inter-arc scattering features. The purple arrows point to the features generated by scattering between bulk states. (e)-(h) Fourier transforms of $dI/dV$ maps taken on surface 2 in the same energy range. The green arrows point to inter-arc scattering features. (i)-(p) Calculated spin-preserving JDOS maps of surface states of both the topmost and the bottommost surfaces in the same energy range. The blue and orange arrows point to inter-arc scattering features. (q) Schematic of inter scattering between two Fermi arcs in the BZ. $q_1$ and $q_2$ represents the head-to-head and tail-to-tail scattering vectors. (r) Experimental $E(q)$ dispersion along $q_x$ axis on two surfaces. The green dashed line marks the dispersion. (s) Dispersion of scattering vectors extracted from QPI patterns and comparison with calculated $q_1$ and $q_2$. 
Chapter 7
Conclusion

In this thesis, we have addressed the impact of point defects on the electronic properties of various types of topological materials. The presence of native defects could often be detrimental for the utilization of topological surface states, as they introduce bulk carriers which hinder the realization of fascinating properties arising from topological surface states. In other situations, however, the presence of native defects can result in observable features associated with intrinsic properties of topological materials. Exotic defects or impurities, on the other hand, can greatly alter the electronic properties of topological materials. They may induce topological phase transition, ferromagnetism or superconductivity.

To be specific, in Chapter 3, we present the experimental studies on the topological insulator Bi$_2$Se$_3$ single crystals and thin films. The prominent native defects in Bi$_2$Se$_3$ single crystals are clearly identified. In particular, Se vacancies and Se interstitial defects are responsible for the spatial fluctuation and the bulk conduction. Their concentrations are significantly affected by the kinetics of synthesis instead of their thermodynamic formation energies. Through the optimization of synthesis process, the formation of native defects is effectively suppressed in the Bi$_2$Se$_3$ single crystal sample, which is approaching the intrinsic limit with the Fermi level inside the band gap. We also reveal the long-lasting p-type doping mystery in Bi$_2$Se$_3$ thin films. We find that the obstacles are the excess n-type defects from the interface between sample and substrate and from the air exposure. By properly protecting the surface of thin films and applying buffer layer, we have achieved p-type Bi$_2$Se$_3$ thin films via compensation doping with calcium. Particularly, our STM results show that the thin
films degrade when they are heavily doped with Ca. Such film degradation is likely responsible for the re-entrance to n-type regime at a high level of Ca doping observed in the transport measurements. The solution to the hole-doping problem of Bi$_2$Se$_3$ thin films is greatly helpful for future development of topological quantum electronic devices.

In Chapter 4, we demonstrate our studies on the the topological phase transition in (Bi$_{1-x}$In$_x$)$_2$Se$_3$. We present compelling microscopic evidence of an inhomogeneous topological phase transition in this system, which is characterized by non-uniform spatial distributions of local band gap and topological surface states. The nanoscale inhomogeneity originates from effective suppression of local spin-orbit coupling and band topology by In defects. Our observations demonstrate that strong disorders can play a significant role in the topological phase transition.

Next we investigate the distributions of electronic defect states of magnetic dopants vanadium(V) and chromium(Cr) in the topological insulator (Bi,Sb)$_2$Te$_3$, which is the parent compound to achieve the quantum anomalous Hall effect. As presented in Chapter 5, the spectroscopic imaging shows very diverse spatial distributions of local defect states of V and Cr. These unique spectroscopic features of the two dopants serve as electronic fingerprints to study the Cr/V-codoped topological insulator thin films. The enhancement of defect states in the overlapping area of neighboring magnetic defects is also systematically studied, which addresses the importance of magnetic defect states on mediating the exchange interactions among magnetic dopants. There are still many interesting features that are not fully understood. Future studies can address these mysteries.

In Chapter 6, we have established the existence of surface states on the type-II topological Weyl semimetal WTe$_2$. We observed a low amount of native defects near the surface of sample. They serve as scattering centers and induce quasiparticle scattering patterns, manifested as the periodic oscillations of LDOS. Through spectroscopic imaging, we directly visualize the quasiparticle interference patterns and
accurately quantify the characteristic scattering vector as a function of energy. The
spin-preserved joint density of state maps are computed via density functional theory
calculations. The good agreement between the calculations and the experiments pro-
vides solid evidence of the presence of surface states on the type-II topological Weyl
semimetal WTe$_2$. 
# List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>2DEG</td>
<td>Two-dimensional electron gas</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>AHE</td>
<td>Anomalous Hall effect</td>
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<tr>
<td>ARPES</td>
<td>Angle-resolved photoemmision spectroscopy</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin zone</td>
</tr>
<tr>
<td>CBM</td>
<td>Conduction band minimum</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<tr>
<td>DOS</td>
<td>Density of state</td>
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<tr>
<td>$E_D$</td>
<td>Energy of Dirac point</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi energy (or Fermi level)</td>
</tr>
<tr>
<td>FS</td>
<td>Fermi surface</td>
</tr>
<tr>
<td>FM</td>
<td>Ferromagnetism/Ferromagnetic</td>
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<tr>
<td>IQH(E)</td>
<td>Integer quantum Hall(effect)</td>
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<tr>
<td>JDOS</td>
<td>Joint density of state</td>
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<tr>
<td>LDOS</td>
<td>Local density of state</td>
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<tr>
<td>LT</td>
<td>Low-temperature</td>
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<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>NI</td>
<td>Normal insulator</td>
</tr>
<tr>
<td>pDOS</td>
<td>Partial density of state</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
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<tr>
<td>QAH(E)</td>
<td>Quantum anomalous Hall (effect)</td>
</tr>
<tr>
<td>QL</td>
<td>Quintuple layer</td>
</tr>
<tr>
<td>QSHE(I)</td>
<td>Quantum spin Hall effect (insulator)</td>
</tr>
<tr>
<td>SOC</td>
<td>Spin-orbit coupling</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscopy (microscope)</td>
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<tr>
<td>STS</td>
<td>Scanning tunneling spectroscopy</td>
</tr>
<tr>
<td>TI</td>
<td>Topological insulator</td>
</tr>
<tr>
<td>TKNN</td>
<td>Thouless, Kohmoto, Nightingale and den Nijs</td>
</tr>
<tr>
<td>TPT</td>
<td>Topological phase transition</td>
</tr>
<tr>
<td>TRIM</td>
<td>Time reversal invariant momenta</td>
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<td>TRS</td>
<td>Time reversal symmetry</td>
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<td>TSS</td>
<td>Topological surface state(s)</td>
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<tr>
<td>TWS</td>
<td>Topological Weyl semimetal(s)</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultrahigh vacuum</td>
</tr>
<tr>
<td>V</td>
<td>Vacancy in Chapter 3 (or vanadium in Chapter 5)</td>
</tr>
<tr>
<td>VBM</td>
<td>Valance band maximum</td>
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<tr>
<td>X.Corr.</td>
<td>Cross correlation</td>
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References


[189] Rajib Batabyal, Noam Morali, Nurit Avraham, Yan Sun, Marcus Schmidt, C. Felser, A. Stern, B. Yan, and H. Beidenkopf. Visualizing weakly bound


