Quantum oscillations in β -Ag₂Te and BiSbTeSe₂ topological insulator systems

Azat Sulaev

2015

Azat Sulaev. (2015). Quantum oscillations in β -Ag₂Te and BiSbTeSe₂ topological insulator systems. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/65529>

<https://doi.org/10.32657/10356/65529>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**Quantum oscillations in β -Ag₂Te and BiSbTeSe₂
Topological Insulator Systems**

Azat Sulaev

Division of Physics and Applied Physics

School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of

Doctor of Philosophy

2015

Acknowledgments

I have been working in Professor Wang Lan's lab since August 2011. At the same time Professor Zhu Weiguang became my co-supervisor. Most important skills required for me to carry out experimental procedures in the lab were taught by prof. Wang. He showed me lot of new experimental techniques, provided necessary theoretical background and advised in every matter I have encountered during my research life. His high expectations and values for the research made me improve in every aspect; experimental ability, theoretical knowledge, and interpersonal skills. I have gained lot of valuable education during my period under prof. Wang.

There are lot of people I've encountered during my postgraduate life, and their contribution has given me immeasurable benefits. Professor Yuan Ping Feng and their student Qingyu Wu from National University of Singapore performed the band structure calculation of Ag_2Te . TEM characterization of the Ag_2Te was carried out by professor Ming-Yong Han and his student Shuang-Yuan Zhang from Institute of Materials Research and Engineering. We also got help from Professor Yu Ting, Caiyu Qiu and Zhi-Peng Li from Nanyang Technological University to prepare Ag_2Te samples for TEM characterization. Professor Zhu Weiguang from Nanyang Technological University has assisted me in the photolithography fabrication of the devices for my project. Professor Kie Leong Teo from National University of Singapore, Professor Shun-Qing Shen from the University of Hong Kong, Professor Sergey Ereameev from Tomsk State University and Professor Yoshiyuki Kawazoe from Tohoku University provided contribution in the theoretical analysis of my work. Also Professor Lei Shen from National University of Singapore with his students Minggang Zeng and Yuan Ping Feng developed theoretical model for BiSbTeSe_2 anisotropic magnetoresistance. When I arrived to NTU, Professor Wang Lan's group consisted of Ph. D.

students Ke Chang, Xia Bin, Ren Peng, Ho Hui Wen, and project officers Liu Peng and Cho Soon Khuen, later FYP student Lim Qing Hua also joined us. All these people were around me in my beginnings and provided lot of help. Notably Ke Chang, Lim Qing Hua and Ho Hui Wen contributed in the designing of the CVD growth for Ag_2Te . Cho Soon Khuen, Liu Peng and Ho Hui Wen assisted in the characterization of my samples, mainly in AFM and SEM. Ren Peng and Xia Bin also contributed in the designing transport measurement in PPMS and solving problems related to it. Notably Ren Peng wrote Lab View programs required to carry out certain measurements in PPMS.

Finally, the constant support from my family has helped me to overcome all obstacles and difficulties I have encountered in my life.

This work was supported by the Ministry of Education of Singapore (Grant NO: MOE2010-T2-2-059) and the Singapore National Research Foundation (RCA-08/018).

Publication List

1. A. Sulaev, P. Ren, B. Xia, Q. H. Lin, T. Yu, C. Y. Qiu, S. Y. Zhang, M. Y. Han, Z. P. Li, W. G. Zhu, Q. Y. Wu, Y. P. Feng, L. Shen, S. Q. Shen, and L. Wang, “Experimental evidences of topological surface states of β -Ag₂Te”, *AIP Advances* **3**, 032123 (2013)
2. A. Sulaev, M. G. Zeng, S. Q. Shen, S. K. Cho, W. G. Zhu, Y. P. Feng, S. V. Eremeev, Y. Kawazoe, L. Shen and L. Wang, “Electrically tunable in-plane Anisotropic Magnetoresistance in Topological Insulator BiSbTeSe₂ devices”, *Nanoletters* **15**, 2061–2066 (2015)
3. A. Sulaev, W. G. Zhu, K. L. Teo and L. Wang , “Gate-tuned quantum oscillations of topological surface states in β -Ag₂Te” , *Scientific Reports* **5**, 8062, (2015)
4. B. Xia, P. Ren, A. Sulaev, Z. P. Li, P. Liu, Z. L. Dong and L. Wang, “Anisotropic magnetoresistance in topological insulator Bi_{1.5}Sb_{0.5}Te_{1.8}Se_{1.2}/CoFe heterostructures ”, *AIP Advances* **2**, 042171 (2012)
5. B. Xia, P. Ren, A. Sulaev, P. Liu, S. Q. Shen, L. Wang, “Indications of surface-dominated transport in single crystalline nanoflake devices of topological insulator Bi_{1.5}Sb_{0.5}Te_{1.8}Se_{1.2}”, *Phys. Rev. B* **87**, 085442 (2013)
6. J. Y. Ou, J. K. So, G. Adamo, A. Sulaev, L. Wang and N. I. Zheludev, “Ultraviolet and visible range plasmonics in the topological insulator Bi_{1.5}Sb_{0.5}Te_{1.8}Se_{1.2}”, *Nat. Comm.* **5**, 5139 (2014)

Quantum oscillations in β -Ag₂Te and BiSbTeSe₂ Topological Insulator systems

by Azat Sulaev

Under the supervision of Assoc. Prof. Wang Lan

ABSTRACT

In this thesis we are going to demonstrate that β -Ag₂Te is a new topological insulator system with high electric field tunability and mobility. Our first-principles calculations show that β -Ag₂Te is a topological insulator with a gapless Dirac cone with strong anisotropy. Observation and analysis of the 2D SdH oscillations and Aharonov-Bohm oscillations in β -Ag₂Te devices confirm the existence of surface states. Highly anisotropic topological surface states of β -Ag₂Te suggest that the material is a promising material for fundamental study and future spintronic devices. Also we will report the electric gate tuned in-plane anisotropic magnetoresistance (AMR) in nanoflake devices of topological insulator BiSbTeSe₂ (BSTS). The AMR in BSTS is found to larger than that of transition metals, and shows tenability from negative to positive gradually when the Fermi level is manipulated to cross over the Dirac point by an applied gate electric field.

Table of Contents

Chapter 1. Topological Insulator Theory	1
1.1 Quantum Hall Effect	1
1.2 Quantum Spin Hall Effect	4
1.3 3D Topological Insulators	8
1.4 Quantum Oscillations	10
1.5 Weak Localization	22
1.6 Magnetic Effect on Quantum interference	27
1.7 The concept of spintronics and spin polarization	31
1.8 Anisotropic magnetoresistance	34
Chapter 2. Experimental procedures	38
2.1 CVD synthesis of the Ag ₂ Te nanoribbons	38
2.2 Material characterization	46
2.2.1 Scanning Electron Microscopy	46
2.2.2 Atomic Force Microscopy	51
2.2.3 Transmission Electron Microscopy	53
2.3 UV Photolithography	56
2.3.1 Substrate preparation	58
2.3.2 Photoresist coating	61
2.3.3 Prebake	62
2.3.4 Align and expose	63
2.3.5 Postbake	68
2.3.6 Second exposure	69
2.3.7 Developing	69
2.3.8 Contact deposition and Magnetron Sputtering System	71
2.3.9 Lift-off process	74

2.3.10 Photolithography parameters used in our projects	76
2.4 Electrical Measurements	77
2.4.1 Electrical measurement setup	80
2.4.2 Aharonov – Bohm oscillations	82
2.4.3 Ag ₂ Te thin film measurements	85
2.4.4 Anisotropic magnetoresistance measurements	86
Chapter 3. Aharonov – Bohm quantum interference in Ag ₂ Te nanowires	89
3.1 Introduction	89
3.2 Band structure calculation	91
3.3 Device fabrication and characterization	93
3.4 Aharonov – Bohm oscillations	99
3.5 Ambipolar gate electric field effect	107
3.6 The shape of R(T) curves vs cross section areas	110
3.7 Conclusion	112
Chapter 4. Gate tuned quantum oscillations of topological surface states in β -Ag ₂ Te	115
4.1 Introduction	115
4.2 Temperature and gate voltage dependence	117
4.3 Berry phase obtained from SdH oscillations	119
4.4 SdH oscillations with gate	126
4.5 The voltage dependence of MR	134
4.6 Conclusion	136
Chapter 5. Electrically tunable in-plane anisotropic magnetoresistance in nanoflakes devices of topological insulator BiSbTeSe ₂	139
5.1 Introduction	139
5.2 Gate voltage dependence of BiSbTeSe ₂	142
5.3 Theoretical model	153
5.4 Conclusion	162
Chapter 6. Future works	167

Chapter 1. Topological Insulator Theory

This chapter covers all essential theoretical review necessary for the analysis of the experimental data obtained in our projects. Mainly we will cover the Quantum Hall Effect, Quantum Spin Hall Effect and their relation to topological insulators. Also topics on weak localization, spintronics, and anisotropic magnetoresistance will be explained.

1.1 Quantum Hall Effect

The Hall Effect was discovered by the Edwin Hall in 1879, who was a graduate student at the Johns Hopkins University. Hall was doing research on the effect of the magnetic field on the conductors, which was inspired by the assertion of the James Clerk Maxwell about the deflection of the current by magnetic field. Edwin Hall designed a setup, which is known as original Hall setup, using a gold leaf instead of a commonly used metal conducting bar. This design helped him to discover the effect on the charge distribution by external magnetic field. This can be observed by the change of transverse Hall voltage on the lateral sides of the conductor with the change of magnetic field or current. But the most important discovery made by Edwin Hall was the relation of the Hall voltage to the material properties of the conductor. Thus Hall Effect is one the crucial tools in the characterization of the charge carriers in the conductors. ¹

At the time of Edwin Hall's experimental results the charge carriers haven't been yet discovered experimentally. Thus people had no clear understanding of the effect, which required the knowledge of the quantum mechanics. In 1930 Landau showed that the quantum electrons under the external magnetic field acquire quantized cyclotron orbits, which leads to the discrete energy levels that could be occupied by the electrons.² Later it was predicted that the quantization of the Hall conductance is also possible. In 1980, Klaus von Klitzing

performed experimental measurements regarding the Hall conductance of the 2D electron gas in a semiconductor material. The experiments were carried out at low temperatures with applied high magnetic field. Von Klitzing discovered that the quantum conductance of the high-mobility 2D electron gas shows a staircase like behaviour as a function of the magnetic field.³ These flat Hall conductance plateaus were found to have precise quantized values, which are integer multiplied by fundamental constant

$$\frac{e^2}{h} = \frac{1}{25812.8075720} \Omega^{-1} \quad (1.1.1)$$

Though the quantization of the Hall conductance was predicted earlier, so precise experimental values obtained from the experiments were not anticipated, because it wasn't affected by the material properties, impurities, geometry of the experiment and etc. This suggests that the integer quantum Hall effect has topological nature.^{4, 5}

Since the quantization of the Hall conductance was quantum phenomena, theorists had tried to develop theories to understand its aspects. Laughlin's gauge argument was one of the major contributions to the theoretical analysis of the quantum Hall phenomena. He took into the consideration that the data was obtained at low temperatures, which allowed him to treat the system and its Hamiltonian evolution in terms of wavefunctions. The calculations carried out by him showed that the electron charge transport taking place in the system gives rise to the Hall conductance in the units of e^2/h . Despite the given work gives the clear understanding of the quantization of the Hall conductance, it wasn't able to explain why the charge transferred is integer multiplied by e .⁶

One of the important concepts in the theory of the topological phases is the Berry phase. This feature has been overlooked in the quantum mechanics for more than a half a century since quantum mechanics has been introduced. In 1981, Michael Berry discovered that the quantum system subjected to an adiabatic evolution acquires an additional phase factor. This phase factor is of geometrical origin, known as Berry phase.⁷ This additional phase was found

to be non-integrable depending only on the geometry of the quantum system, thus it was suggested not to be neglected. Previously acquired geometrical phase has been neglected in the theoretical calculations, but Berry pointed out that this phase is gauge invariant, meaning it couldn't be gauged away.⁸ The theoretical calculations of the accumulated phase factor after the quantum system completes an adiabatic cyclic path showed that Berry phase would be

$$\mathbf{B}_n(\mathbf{R}) = \nabla_R \times \mathbf{A}_n(\mathbf{R}), \quad (1.1.2)$$

where Berry connection is defined as⁷

$$\mathbf{A}_n(\mathbf{R}) = -i \langle n, \mathbf{R} | \nabla_R | n, \mathbf{R} \rangle \quad (1.1.3)$$

Geometrical interpretations are important in the case of relating quantum Hall effect to its topological nature, because geometry and topology are closely related subjects. Topological systems are generally parameterized by a topological invariant g , e.g. $g=1$ for a torus. In the given example any geometrical surface deformations of a torus would still lead to the same topology of torus, unless you make an extra hole on the surface. Similarly, quantum systems could also be linked to the topology. We can consider a Hamiltonian $H(\Phi, \theta)$, which depends on two angular parameters. The eigenstates of this quantum-geometrical system could be defined by the Φ and θ . So linking these parameters to the topology, we must be able to get a topological invariant for our system. This topological invariant is called Chern number or TKNN invariant.⁴ Like in the example of a torus, our Chern number is also an integer as topological parameter. Earlier Berry phase was introduced as an additional phase factor acquired by quantum system after making adiabatic cycle. We can consider one closed loop for the wavefunction to travel around. Then the complete cycle could be performed either on the inside surface of the loop, or outside surface. In the end these two different cycles would provide a different phase, which divided by 2π gives us Chern number, an integer value.

Chern number, which is identified as topological invariant, is not affected by small perturbations in the Hamiltonian of the system. When the Berry curvature of the given system diverges strongly, the Chern number is not defined. Since the value of Chern number is integer, it can't have continuous transition to another value, thus we will be observing plateau like transitions from one integer value to another.

The theoretical progress regarding the topological sorting of the condensed matter systems has provided an important tool in the classification of the different kind of new phenomenon. The Quantum Hall Effect, in fact, is the first system that was characterized by a topological order as a way to distinguish this particular effect.

1.2 Quantum Spin Hall Effect (QSHE)

The Quantum Hall Effect occurs under strong external magnetic field applied to the system, which generates Landau quantization. The electrons in the 2D electron gas system are forced to revolve around the magnetic field, which impose a Lorentz force on electrons. But as you can see from Fig. 1.2.1(a) the electrons near the edge of system cannot complete the loop driven by magnetic field. Thus these electrons will be forced to go propagate along 1D channel after being bounced by edge states. This phenomena lead to another electronic state at the edge, because the given edge electrons won't have other option but to travel along the edge, i.e. their energy state will be quantized. Given the sample with Quantum Hall Effect, we will observe two different 1D current channels at the top and bottom edges, propagating at opposite directions. Important property of these channels is that the electrons are not allowed to bounce back by impurity, deformation or etc. This in the end provides a charge transport without dissipation.

Since in the case of Quantum Hall Effect we were able to separate the charge transport into two opposite direction currents, would not be more intriguing to separate the charge

transport based on their spin direction, like in Fig. 1.2.1(b). This kind system is called a Quantum Spin Hall Effect. For the Quantum Hall Effect to be observed we require an external magnetic field, while Kane and Mele suggested that the same purpose could be carried out using strong spin-orbit interaction. Spin-orbit coupling is the interaction of the electron's spin with its orbital motion through space. If the material under consideration contains a strong spin-orbit interaction, we might be able to observe the QSHE even in the absence of the external magnetic field. Since in the spin-orbit coupling you have to consider the direction of the electron's spin, eventually it will lead two different spin-up and spin-down channels at the edge of the system.

Figure 1.2.1. Schematic representation of edge states. a) In the Quantum Hall State the electrons are set to circular orbital motion by external magnetic field B , but the electrons at the edge cannot complete full orbit that leads to conduction along the edge. b) For the Quantum Spin Hall State we have two states with spin-up and spin-down electrons moving in opposite directions. (Kane *et al.*).⁴⁸

QSH state behaves like an ordinary insulator with gap between conduction and valence bands, but here we have as well the conduction edge states with spin-up and spin-down electrons. For the given sample with QSHE the Hall conductance is zero, because the

electrons with opposite spin directions eventually cancel each other. In the QH state we have stated a unique property of the states to carry out dissipationless transport, unlike QH state in the QSHE there are two channels at the edge. Despite the electrons moving in two channels, QSH state as well protects its electrons from backscattering. The main role in this phenomenon is played by time-reversal symmetry, which successfully switches the propagation and spin direction of the electrons.

The charge carriers travelling inside the system could be scattered by any impurity they face in their way. But as we mentioned earlier both QH and QSH states require a perfect transmission of the electrons in the edge states. This condition for QSH is conserved unless the impurities in the system are magnetic, because they will destroy the time-reversal symmetry. The QSH state contains two channels with spin-up and spin-down electrons, also named Kramers pairs, so there are only two possible states for the electrons to exist. If the spin-up electron is scattered back, for it to travel in opposite direction to original it's also required to change spin direction. Imagine an electron spin which encounters an impurity along its path, Fig. 1.2.2 This electron spin has two choices to be scattered back and flipped by this non-magnetic impurity: it can rotate clockwise around the impurity or anti-clockwise, thus the phase change for this electron spin will be $+\pi$ and $-\pi$ respectively. Both cases have different direction of rotation giving the spin 2π difference. In the quantum mechanics if the electron spin completes 2π rotation, it will end up having wavefunction with negative spin - $1/2$. Meaning that if two wavefunctions follow the path of the given example in the end they will interfere destructively, which gives us only electrons that will propagate forward, rather than being scattered back by a non-magnetic impurity.⁹

In our example we have discussed about 1D system with single pair of spin-up and spin-down electrons travelling in opposite directions. But imagine if there were several pairs spin-up and spin-down electrons in the same system. If 1D system contains two spin-up

electrons channels travelling in opposite direction, then impurities will be allowed to scatter electrons without switching its spin direction. This situation will easily allow back scattering, which means “dissipationless” transport is no longer valid. The important aspect for the QSH state is to have odd number of spin-up and spin-down pairs, which is also called Z_2 invariance. In this case QSH state will have edge states that are protected by time-reversal symmetry from non-magnetic impurities.

Figure 1.2.2. The electrons in the Quantum Spin Hall State can be scattered by the impurities in two possible ways. In the clockwise scattering of the spin state the spin rotates by π (blue line), while in the anti-clockwise scattering the phase will change by $-\pi$ (red line). The phase difference between the spins will give us destructive interference. (Qi *et al.*)⁹.

Few years later after the theoretical prediction of the topological insulators the group in University of Wurzburg discovered experimentally the first 2D topological insulator.¹³ The group led by L. Molenkamp fabricated the HgTe quantum well structures sandwiched between layers of $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ using molecular-beam epitaxy. Since we have two conducting edge states, each of them will be contributing e^2/h to the total conductance. When the thickness of the quantum well was varied, the conductance of the sample was measured to change from small value to the $2e^2/h$, which indicates that the system made a transition from insulating state to the Quantum Spin Hall state. The results were also independent from the variation of the width of the structures, which is expected from these kind of systems.

1.3 3D Topological Insulators.

Another step in the research in the family of topological insulator electronic phases is the 3D topological insulator. Several theorists have already extended their theoretical analysis of the topological insulators from 2D to 3D systems even before the experimental evidences have been given for the existence of the 2D topological insulator. The picture of the 3D topological insulator cannot be viewed in the same perspective of a spin-dependent magnetic field, as 2D topological insulator. They have topological order, which is characterized by four Z_2 invariants instead of one.⁹⁻¹¹ Still the 2D surface of the 3D topological insulator resembles to the 1D edge channels, as we discussed in previous chapter. In the 1D channel the direction of the spin current is along the edge, but on the 2D surface the direction of the electron motion is determined by the spin direction. Thus it would give us 2D metallic surface on the topological insulator material, where the electron spin and propagation directions are locked. The 2D surface states on the 3D systems are also topologically protected from backscattering.

Figure 1.3.1. The surface of the 3D topological insulator. (Kane *et al.*)⁴⁸

From the Fig. 1.2.1(b) we can observe the pair of 1D conducting states crossing from conduction band to valence band near momentum $k = 0$. The dispersion relation of these edge states is linear, which agrees with the theoretical calculation of the surface states using Dirac equation for massless fermions in 1D system. Similar to that it is possible to extend the

theoretical calculation for a 3D topological insulator, i.e. massless Dirac fermion in the 2D system, which will give us a dispersion relation like a single Dirac cone. The crossing point is also located at the TR-invariant point $k = 0$, thus our system is also protected by time-reversal symmetry.

As we mentioned earlier, the 2D QSH was already experimentally demonstrated. In the case of 3D QSH effect it's much more difficult to provide experimental evidences. One of the main issues is interior insulating band gap of 3D topological insulator, though ideally we expect the bulk to be insulator it will still provide small conductivity. This bulk conductivity also interferes with the surface metallic states, thus the experimental results obtained from probing surface states can be also coupled with bulk data. So far the most efficient technique to demonstrate the topological nature of the 3D crystals is the angle-resolved photoemission spectroscopy (ARPES). The advantage of ARPES system is that it can couple with the surface electrons and obtain information about the surface states. It ejects photons into the sample with certain angle, and then electrons at the surface of the material absorb energy enough to break the bonds and escape. The scattered electrons are collected by detector and information about momentum, energy, and spin of these electrons are extracted. Using these information we can construct the electronic band structure of the material and even the spin polarization of the sample.

In 2006 Fu and Kane made a prediction that the alloy $\text{Bi}_{1-x}\text{Sb}_x$ could be a 3D topological insulator.¹¹ They also proposed that this could be proven using ARPES technique by counting number of surface states crossing the Fermi level between two TR-invariant momenta. Later a group led by Hasan from Princeton University conducted an experiment using an ARPES to map the surface states of the $\text{Bi}_{1-x}\text{Sb}_x$.¹⁴ The results obtained showed that the alloy $\text{Bi}_{1-x}\text{Sb}_x$ is indeed 3D topological insulator. The same group later also identified using ARPES that the $\text{Bi}_{1-x}\text{Sb}_x$ hosts specific spin polarization. Analysis of the dependence of electron's spin

direction to momentum led to the conclusion of existence of π Berry phase on the Fermi surface of topological insulator. But the surface electronic structure came out to be more complicated than the theoretical predictions, which led to researchers to look for new topological insulator systems.

Other than $\text{Bi}_{1-x}\text{Sb}_x$ the Fu and Kane have also proposed that HgTe to be a 3D topological insulator.¹¹ But their theoretical calculations were incomplete, because they didn't perform "parity analysis". Later Zhang *et al*, performed necessary theoretical analysis and suggested the Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 should be 3D TIs.¹⁵ He also successfully developed new model of theoretical analysis of the bulk electronic band structure for the topological insulators.¹⁶ These predicted materials are semiconductors with strong spin-orbit interactions. Their bulk energy band gap is relatively large (0.3 eV for Bi_2Te_3), which makes them still effectively insulating even at room temperature. Bi_2Se_3 ¹⁷ and Bi_2Te_3 ¹⁸ were experimentally found to be 3D topological insulators with Dirac cone like electronic band structure, while Sb_2Te_3 ¹⁸ has been confirmed as 3D TI only recently. Another advantage of this class of materials is their simple electronic band structure. These discoveries attracted wide attention of the research society, which put lot of effort to analyse experimentally the electrical and magnetic properties of this new class of materials.

1.4 Quantum oscillations.

Quantum oscillations are the common name for the various quantum phenomena observed mainly in the crystalline solids, when the external magnetic field is manipulated.¹⁹ This is related to the motion of the charged electrons under the uniform magnetic field. You can consider the electron on the 2D plane xy , where there is also a constant magnetic field pointing in the z direction. The magnetic field will generate the Lorentz force on the charged particle, forcing it to move in spirals. Eventually the Lorentz force will be balanced by the

centrifugal force. The cyclotron orbits, which electrons can occupy under the constant magnetic field, are quantized. Since the energy values of the electrons in the cyclotron motion are related to cyclotron radius, this gives us understanding that electrons can occupy the cyclotron orbits only when they have certain energy value. These discrete energy values are called Landau levels. Landau levels are given by equation²⁰

$$E_n = \hbar \omega_c \left(n + \frac{1}{2}\right) \quad (1.4.1)$$

$$\omega_c = \frac{eB}{mc} \quad (1.4.2)$$

where $\hbar$ is the Plank's constant divided by 2π , $n = 0, 1, \dots$, the states that constitute to the n -th Landau level. The number of electrons that can occupy certain Landau level is directly proportional to the strength of the magnetic field.

Figure 1.4.1. Schematic illustration of Landau quantization. (Chou *et al.*)⁵⁰

Figure 1.4.2 (a) Partially-filled 2D Dirac cone; μ as the Fermi level. (b) Landau quantization of the Dirac cone under low magnetic field. (c) In a higher magnetic field, the spacing between LLs increases as $\sqrt{B}$, and fewer LLs are filled. (d) Schematic behavior of σ_{xx} and σ_{xy} in the quantum Hall regime of 2D Dirac fermions; the arrows indicate the cases in (b) and (c). (Ando)⁴⁹

When the external magnetic field is the zero the density of states (DOS) will be constant with the energy. While external magnetic field will generate Landau quantization and the density of states will form a series of uniformly distributed peaks. The density of states in the Landau quantization ideally must periodic δ functions, but scattering of electrons transforms them into the broadened peaks.

One of the prominent quantum oscillations that could be observed the crystalline solids is the Shubnikov – de Haas (SdH) oscillations. It is a quantum phenomenon that takes in the conductivity of the material when external magnetic field is applied. The conductivity of the

material is related to the number of states available in energy for electrons to scatter into. The highest conductance occurs whenever Fermi level and Landau level lined up with each other. This is because the density of states is a maximum at the centre of the Landau level. In the similar way, when the Fermi energy is between two adjacent Landau levels, we will observe decrease in the conductance, since density of states has its minimum at that point.

Due to the periodic nature of the density of states in the Landau quantization, it's possible to make the conductance to oscillate. We can modulate the gate voltage, which subsequently will shift the Fermi energy, so that conductance will exhibit the fluctuations as Fermi level will cross through a series of Landau levels. This would give us quantum oscillations with same period, because the separation of Landau levels will be constant under the unchanged magnetic field. Another way to observe quantum oscillations is to vary the magnetic field. In this case the Fermi energy position will remain unchanged. But the spacing of the Landau levels depends on the strength of the magnetic field (Eq. 1.4.1). With increasing magnetic field the energy levels will gain larger spacing between each other. While Landau levels will start to shift with changing magnetic field, they will subsequently pass through the Fermi energy as well. Thus again we can observe the quantum oscillations in the conductance of the material. Both these quantum phenomena are referred as SdH oscillations.

The SdH oscillations, as already have been mentioned, are periodic, while the amplitude and the period of the oscillations is changing with increasing magnetic field. The conductivity oscillations in SdH phenomenon are generated as a function of $1/B$, where the longitudinal part is given by¹⁹

$$\Delta\sigma_{xx} \sim \cos \left[2\pi \left(\frac{F}{B} + \frac{1}{2} - \beta \right) \right] \quad (1.4.3)$$

where F is the oscillation frequency, and β is a phase shift.

The broadening of the Landau levels happens due to the thermal and disorder scatterings. To observe the SdH oscillations clearly, it is required to have the broadening of energy levels as small as possible. The spacing between two adjacent Landau energy levels is $\hbar\omega_c$, while thermal broadening is kT and disorder induced scattering gives $\hbar/\tau$ broadening, where k is Boltzmann's constant, T is a temperature, and τ is a momentum relaxation time. In the measurement for probing SdH oscillations we require that Landau level spacing $\hbar\omega_c$ would be larger than kT and $\hbar/\tau$, otherwise the two neighbour Landau levels will overlap. The more Landau levels overlap the smaller periodicity can be observed in the conductance of the device. At lower temperatures the thermal broadening will reduce, and a material with high mobility would provide smaller broadening due to scattering. If we set conditions for the SdH measurements to carry out as $\hbar\omega_c > kT$ and $\hbar\omega_c > \hbar/\tau$, we can get the $T < 1.3B/(m^*/m_0)$ K and $\mu > 10^4/B$ cm²/V.s, where m_0 is the free electron mass, and m^* is effective mass of electron.

From experimental set of data it's possible to identify the frequency of oscillations and phase shift β . This information could be obtained from the analysis of the LL fan diagram. In this plot the values of $1/B_N$, obtained from the minima of oscillations periods of $\Delta\sigma_{xx}$, are plotted versus the N . When one Landau level passes through the Fermi energy level, it will constitute to the one complete period of oscillation in the $\Delta\sigma_{xx}$ observed and one period is equal to phase 2π ^{19, 21}. Thus the N -th Landau level comes with a $2N\pi$ phase factor. But for the case of Dirac fermions there is also zeroth Landau level. Thus the filling factors in the energy levels will be $N + \frac{1}{2}$, instead of N . The phase factor from the Eq. 1.4.3 must follow the equality

$$2\pi \left(\frac{F}{B_N} + \frac{1}{2} - \beta \right) = (2N - 1)\pi \quad (1.4.4)$$

This equation tells us that if we plot $1/B$ versus N , then we must get the linear relationship with a slope F . Since our theoretical fitting is linear, we can extrapolate the fitting line

beyond the experimental data. If $1/B_N \rightarrow 0$, then the phase factor β can be estimated from the LL fan diagram plot. In the case of Dirac fermions the expected value of β is $1/2^{19, 21}$. In this way we can distinguish from the SdH oscillations the type of fermions contributing to the conductivity of the material.

This method of obtaining the phase factor β should be carried out carefully. In early analyses of the LL fan diagram there were lot of confusions on how to carry out calculations correctly. Because it wasn't clear how to assign indexing integer N , whether to the minima of the conductivity σ_{xx} , or to the minima of the resistivity ρ_{xx} .²²⁻³⁰ Thus most of the early theoretical calculations on the LL fan diagram of SdH quantum oscillations were based on the methods used in the graphene system.³¹⁻³² Later it was suggested by Xiong *et al.* to use the minima of the σ_{xx} in the construction of the LL fan diagram, which would provide the correct derivation of the phase factor β .³³ To understand why this method is correct, we can analyse the resistivity tensor relation to the conductivity tensor. In solids this relation is given by the equation

$$\begin{aligned} \begin{pmatrix} \rho_{xx} & \rho_{xy} \\ \rho_{yx} & \rho_{yy} \end{pmatrix} &= \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ -\sigma_{xy} & \sigma_{xx} \end{pmatrix}^{-1} \\ &= \frac{1}{\sigma_{xx}^2 + \sigma_{xy}^2} \begin{pmatrix} \sigma_{xx} & -\sigma_{xy} \\ \sigma_{xy} & \sigma_{xx} \end{pmatrix} \end{aligned} \quad (1.4.5)$$

For the case of graphene the condition $\sigma_{xx} \ll \sigma_{xy}$ can be applied, which also the case for all low carrier density semiconductors. Using this condition the Eq. 1.4.5 can be approximated to obtain $\rho_{xx} \approx \sigma_{xx}/\sigma_{xy}^2$, thus the minima of the ρ_{xx} and σ_{xx} will coincide, because they are related to each other. So for the graphene the consideration of the minima point in ρ_{xx} to assign the integer N was correct. But the 3D topological insulator crystal the same condition cannot be applied, mainly because of the bulk contribution to the conductivity channel. Consider the opposite situation $\sigma_{xx} \gg \sigma_{xy}$ for the earlier example of low carrier density systems. For the condition our resistivity ρ_{xx} will come out to be $\rho_{xx} \approx \sigma_{xx}^{-1}$. This

would give us the minima of the ρ_{xx} coinciding with the maxima in the σ_{xx} . But making these kind approximations for the complex systems like TI might be tricky and lead to the large deviations in the derivation of the phase factor β . The reliable way for accurate construction of LL fan diagram is to measure both ρ_{xx} and ρ_{xy} , then calculate the values of σ_{xx} and σ_{xy} . But of course the measurement technique must be designed carefully to effectively separate the ρ_{xx} and ρ_{xy} from each other.

Figure 1.4.3 (a) SdH oscillations observed in a 10-nm-thick MBE-grown Bi_2Se_3 film. (b) LL fan diagram constructed from the analysis of the σ_{xx} data measured at 1.6 K and $\theta = 0^\circ$. (Upper inset) The minima peaks are assigned to the integer N values. (Lower inset) Fourier analysis of the given data. (Ando)⁴⁹

The further analysis of the SdH oscillations can as well provide more information regarding the nature of this quantum phenomenon. It can be identified whether the SdH oscillations are related to the 2D surface state of the topological insulator. The oscillation frequency in the Eq. 1.4.3 is given by Onsager relation as¹⁹

$$F = (\hbar c / 2\pi e) \pi k_F^2 \quad (1.4.6)$$

where k_F is the Fermi wavevector. As we have already mentioned in the analysis of the LL fan diagram, that it's possible to derive the F from the slope of the LL fan diagram plot. In this way we can calculate the value of the wavevector k_F . This information can be further exploited in the determination of the surface carrier density in the topological insulator. If we consider the 2D surface state for topological insulator then our relation will be

$$n_S = \frac{1}{(2\pi)^2} \pi k_F^2 \quad (1.4.7)$$

Since the topological insulator has spin locking on the Fermi surface the multiplication by 2 has been dropped, which accounts for the spin degeneracy. These theoretical evaluations are correct if the contribution from the bulk conductivity can be neglected. But currently most of the 3D topological insulator systems have their surface state affected significantly by the bulk states of the material. However it's possible to carry out calculations of bulk carrier density n_{3D} in the similar way. For the 3D case we have to consider that the Fermi surface has different range in different directions, which will give us the shape of an ellipsoid with different Fermi wavevector along three different axes k_F^a, k_F^b , and k_F^c . Then SdH oscillations must be measured with magnetic field along three principal axes, later wavevector values can be derived from the analysis of the LL fan diagram. The equation for the charge carrier density for 3D bulk state will be

$$n_{3D} = \frac{2}{(2\pi)^3} \frac{4\pi}{3} k_F^a k_F^b k_F^c \quad (1.4.8)$$

One of the simple techniques proposed to identify whether the SdH oscillations have 2D nature^{22-25, 27, 34} is to perform measurements of SdH oscillations at different angles between

magnetic field direction and surface plane normal. Depending on the angle these SdH oscillations will have different oscillation frequency F . If the constructed plot of F versus θ has evolution of frequency F as a function of $\sim 1/\cos\theta$, then this gives a strong indication for 2D nature of SdH oscillations.²³ However the measurements should be taken importantly at larger angles, though the intensity of the SdH oscillations is weak at large angles. The reason is that the 3D bulk state can also have the elongated Fermi surface, where one of the Fermi wavevectors along one of the axis is much smaller than of other principal axes. Thus at small angles this elongated Fermi surface will also provide the oscillation frequency F as a function of $\sim 1/\cos\theta$. When the angle between magnetic field and surface plane normal is 90° , the SdH oscillation must disappear, while only bulk states will be contributing to the SdH oscillations.

Another possibility in the analysis of the SdH quantum oscillations is to estimate the values of the cyclotron mass m_c . For this purpose the measurements of the SdH oscillations must be performed at different temperatures. The obtained results can be processed using the relationship given in the Lifshitz-Kosevich theory¹⁹

$$\Delta\sigma_{xx} = A_0 R_T R_D R_S \cos \left[2\pi \left(\frac{F}{B} + \frac{1}{2} - \beta \right) \right] \quad (1.4.9)$$

where A_0 is a constant, R_T , R_D , and R_S are the temperature, Dingle, and spin damping factors, respectively, given by the equations

$$\begin{aligned} R_T &= 2\pi \frac{k_B T / \hbar \omega_c}{\sinh[2\pi^2 (k_B T / \hbar \omega_c)]} \\ R_D &= e^{-2\pi^2 k_B T_D / \hbar \omega_c} \\ R_S &= \cos \left(\frac{1}{2} \pi g m_e / m_c \right) \\ T_D &= \frac{\hbar}{2\pi k_B \tau} \end{aligned} \quad (1.4.10)$$

where T_D is Dingle temperature, g is the electron g -factor, τ is the quantum scattering time and m_e is free electron mass. With varying temperature the only coefficient that will be

affected is the R_T , given the condition that magnetic field will remain constant. This will allow us to use the temperature dependence to calculate the cyclotron frequency w_c . The relationship of the cyclotron frequency with cyclotron mass was given early as $m_c = eB/cw_c$. There is one way to exploit the calculated m_c and confirm whether experimental data matches with theoretical. We can transform the given values of the m_c into the Fermi velocity v_F , which also can be obtained experimentally from the ARPES using a slope of the Dirac dispersion. In order to calculate the v_F , the equation for the m_c can be derived from energy dispersion relation

$$m_c = \frac{\hbar^2}{2\pi} \left(\frac{\partial A(E)}{\partial E} \right)_{E=E_F} \quad (1.4.11)$$

where $A(E)$ is the area in the k -space the electron cyclotron orbit encloses. For the 2D Dirac fermions we have to consider that $A(E)$ is also has 2D shape on the Fermi surface, thus it can be estimated to be $A(E) = \pi k_F^2$. Since we already know that energy dispersion relation for Dirac-like fermions is $E(k) = \hbar v_F k$, the cyclotron area can be transformed as a function of E_F into $A(E_F) = \pi E_F^2 / (\hbar v_F)^2$. Substituting the later equation into the Eq.1.4.11 the final equation $m_c = E_F / v_F^2 = \hbar k_F / v_F$, where the final manipulations would lead to $v_F = \hbar k_F / m_c$. So applying this formula for the calculation of the v_F , since we already know m_c , the derived value can be compared to APRES obtained value.

Another application of the SdH oscillations is the possibility to determine the quantum scattering time τ , which is given in the Dingle temperature equation. Thus first of all, one has to perform necessary calculations using the Eq.1.4.10 to determine the value of the T_D . For these calculations another method is required, called Dingle analysis, where the temperature is kept constant while the variable is magnetic field. For the Dingle analysis we have to construct the plot of $\ln[AB \sinh \alpha T / B]$ against $1/B$, where A is the amplitude of the SdH oscillations with magnetic field, and $\alpha = 14.7 (m_c / m_e)$ T/K. The slopes of this graph will

be equal to T_D , because the Eq. 1.4.9 is giving this conclusion. By this method the raw data from the experiments can be used to obtain T_D , which later can be converted into τ . This scattering information for the Dirac fermion further can help us to estimate the mean free path and even the carrier mobility, that are given by $\ell^{SdH} = v_F \tau$ and $\mu^{SdH} = e\tau/m_c = e\ell^{SdH}/\hbar k_F$.

The first experimental observation of the SdH oscillations in the 3D topological insulators was made in 2009 by Taskin and Ando, in the device of $\text{Bi}_{1-x}\text{Sb}_x$.³⁵ They were able to verify that the phase factor for the quantum oscillations coming from the 2D Fermi surface indeed indicate the π Berry phase. The further analysis of the 2D component of the SdH oscillations provided the experimentally calculated values of $m_c = 0.0057m_e$, $T_D = 6.7\text{ K}$, and $n_S = 1.4 \times 10^{10}\text{ cm}^{-2}$. The small values for m_c and n_S are in fact the characteristic fingerprint of the Dirac fermions. But for this experiment the 2D component of the SdH oscillations turned out to be larger than expected. This is despite the density of 3D bulk electrons is significantly larger than the surface electrons, which distorts the understanding whether the obtained results were coming from the outer surface of the 3D topological insulator.

Soon another publication was made regarding the observation of SdH quantum phenomenon in 3D topological insulators, Bi_2Se_3 and Bi_2Te_3 , by Analytis *et al.*²⁶ and Qu *et al.*²³, respectively. The same method was applied to confirm the 2D nature of the SdH oscillations as in previous work³⁵, which is to analyse the angular dependence of the SdH oscillation frequency. Since the APRES results regarding these 3D topological insulators were already known³⁶⁻³⁸, these groups were able to confirm that their obtained quantum oscillations contained 2D origin.

1.5 Weak Localization

With the development of the methods and technologies good enough to fabricate high quality thin films, single crystals, etc., it was possible to verify or falsify many predictions regarding the theory of electronic properties in the disordered solids. One of the phenomena that consider the quantum interference of the conducting electrons with the defects inside the solid is weak localization.³⁹ As the conducting electrons encounter the defects, impurities, etc. they will experience two types of elementary scattering events. In the first case, the scattered electrons will preserve their energy, which means their temporal variation of the wave function $\exp(i\varepsilon_j t/\hbar)$ will remain unchanged. With the given time τ between two elastic collisions, we can denote the frequency of the elastic scatterings as $1/\tau$. But there is also another type of scattering, which is in contrary to the elastic scattering going to change the electrons energy ε_j and destroy the phase memory of the electron prior to the collision. This type of inelastic collision might occur when electron collides with other electrons or phonons. The frequency of the inelastic scattering is $1/\tau_\varphi$, which also is the probability for the electron to lose its memory. In this topic we are interested in the quantum correction to the electron conductivity, thus we require more elastic scatterings taking place in the system without inelastic scattering. This case can be approximated by the given inequality

$$\tau_\varphi \gg \tau \quad (1.5.1)$$

In the usual case of the classical diffusion electrons are treated as particles being randomly scattered by the impurities or other electrons. Thus we can consider statistical approach in the calculating the probability of the finding electron in particular point in space. But of course the physics of quantum mechanics often deviate from classical, for our case the electron behave like wavefunctions in their motion and their interaction with other electrons, defects,

phonons, etc., provides an additional correction to the metal conductivity estimations. To understand the underlying physics behind these phenomena let us consider the classical approach, where the electron can be found at $t = 0$ at the origin coordinate $\mathbf{r} = 0$. This electron travels around the space with Fermi velocity v_F and could be found at point $\mathbf{r}$ after $t \gg \tau$ with probability

$$p(\mathbf{r}, t) = (4\pi Dt)^{-d/2} e^{-r^2/4Dt}$$

$$r^2 = \sum_1^d x_i^2$$

$$\int p(\mathbf{r}, t) d\mathbf{r} = 1$$

where D is the diffusion coefficient gives as $D = lv_F/d$, d is the dimensionality of the space. The diffusion is caused by continuous scattering of the electron and the probability to find electron again at the origin will continue to decrease with time since the diffusion radius will continuously increase with time

$$\Delta r \approx \sqrt{Dt} \approx l\sqrt{t/\tau} \approx l\sqrt{N} \quad (1.5.2)$$

where $N = t/\tau$ number of collisions that took place within the time t .

If the electron starts from a position $\mathbf{r} = 0$ at $t = 0$, there is a probability to find this same electron in any location after $t > 0$, so it could be found in the same starting position $\mathbf{r} = 0$. Since we are considering the case of elastic scattering, our electron will arrive to starting point without losing its phase memory. However the electron phase memory doesn't last for long, thus we must narrow down our analysis to $t < \tau_\phi$. Now consider the probability $p(0, t)$ of finding the same electron again at the same starting point $\mathbf{r} = 0$ after going through series of scattering events within the time t . From the classical point of view we have to calculate the summation of all possible trajectories that lead back to the origin. But in quantum

mechanics we have to sum the electron wavefunctions, which gives the result as doubled probability to find electron at $r = 0$ compared to classical case.

classical summation $|A_1|^2 + |A_2|^2 = 2A^2$

quantum summation $|A_1 + A_2|^2 = |A_1|^2 + |A_2|^2 + 2|A_1 A_2| = 4A^2$ (1.5.3)

From this analysis we can see that the quantum interference of the electron wavefunctions give the probability doubled than of classical approach.

Figure 1.5.1. Possible closed looped trajectories for the electron diffusion.

The electron wave function properties give higher probability that the electron could be found at the same starting point $r = 0$. This electronic property will give different conductivity in the disordered solid. To evaluate the quantum correction in 3D to the conductivity we can estimate the $d\sigma$ contribution at time dt and later integrate it over time t . Since electrons are constantly getting scattered around their distribution is defined by the diffusion. All the electrons started from the origin could be found inside the volume $(Dt)^{3/2}$,

where D is the diffusion constant. At time dt all the electrons inside the volume $\lambda^2 v_F dt$, which is around the origin, can reach the origin, so these electrons will provide the quantum correction. Our estimation in three-dimensional case could be integrated as follows

$$d = 3: \frac{\delta\sigma_3}{\sigma} \simeq - \int_{\tau}^{\tau_{\varphi}} \frac{v_F \lambda^2 dt}{(Dt)^{\frac{3}{2}}} \simeq - \frac{v_F \lambda^2}{D^{\frac{3}{2}}} \left(\frac{1}{\tau^{\frac{1}{2}}} - \frac{1}{\tau_{\varphi}^{\frac{1}{2}}} \right) \simeq (k_F^2 l)^{-1} \left(\frac{1}{l} - \frac{1}{L_{\varphi}} \right) \quad (1.5.4)$$

$$L_{\varphi} \approx \sqrt{D\tau_{\varphi}} \approx l \sqrt{\frac{\tau_{\varphi}}{\tau}} \gg l \quad (1.5.5)$$

where L_{φ} is the phase breaking length. The integration is carried out starting from time τ , because at this time electron will experience the first collision, and until time τ_{φ} , since after that phase memory will be lost and this is not going to contribute to the quantum correction. Similar equation could be derived for the two-dimensional and one-dimensional cases. If the L_{φ} is larger than the thickness of the sample b , $b \ll L_{\varphi}$, but smaller than the surface area, we can consider that system as two-dimensional. In the one-dimensional case we have thickness and width smaller than the L_{φ} , which means that the electron can be scattered inelastically only along one direction. From the equation (1.5.5) we can see that the quantum correction is related to the $e^2/\hbar$, the same relation can be seen in 2D and 1D cases⁴⁷.

$$d = 2: \frac{\delta\sigma_2}{\sigma} \simeq - \int_{\tau}^{\tau_{\varphi}} \frac{v_F \lambda^2 dt}{(Dt)b} \simeq - \frac{v_F \lambda^2}{Db} \ln(\tau_{\varphi}/\tau) \simeq \frac{1}{(k_F l)(k_F b)} \ln(\tau_{\varphi}/\tau) \quad (1.5.6)$$

$$d = 1: \frac{\delta\sigma_1}{\sigma} \simeq - \int_{\tau}^{\tau_{\varphi}} \frac{v_F \lambda^2 dt}{(Dt)^{\frac{1}{2}} b^2} \simeq - \frac{2v_F \lambda^2}{Db^2} (L_{\varphi} - l) \simeq \frac{1}{(k_F b)^2} \left(\frac{L_{\varphi}}{l} - 1 \right) \quad (1.5.7)$$

The conductivity of the sample in the equations carries the negative sign, as we discussed that electrons will be more likely to be found at the starting origin meaning that they prefer sit at starting point instead of contributing to the total conductivity. Since with decreasing temperature the elastic scatterings start to resurface, then the conductivity will continue to decrease with the temperature. But of course at higher temperatures our assumptions don't hold, because the energetic electrons will take part only in inelastic scatterings. At very low

temperature $T \rightarrow 0$, the $L_\varphi \rightarrow \infty$ and $\tau_\varphi \rightarrow \infty$. If we apply these values to the $\delta\sigma_i/\sigma$ equations, then we can see that $\delta\sigma_1$ and $\delta\sigma_2$ diverge to the infinity at $T \rightarrow 0$, while $\delta\sigma_3$ has some limit. In this case $\delta\sigma_i$ will be larger than the σ , implying that in the end we'll obtain a negative value for the conductivity, which doesn't make any physical sense. It's more convenient to use the absolute values of the conductivity corrections $\Delta\sigma_d = \delta\sigma_d b^{3-d}$, which will give us

$$d = 3: \Delta\sigma_3 \approx -const. + \left(\frac{e^2}{h}\right)L_\varphi^{-1} \quad (1.5.8)$$

$$d = 2: \Delta\sigma_2 \approx -\left(\frac{e^2}{h}\right)\ln\left(\frac{\tau_\varphi}{\tau}\right) \approx -2\left(\frac{e^2}{h}\right)\ln\left(\frac{L_\varphi}{l}\right) \quad (1.5.9)$$

$$d = 1: \Delta\sigma_1 \approx -\left(\frac{e^2}{h}\right)L_\varphi \quad (1.5.10)$$

These equations all have $e^2/\hbar$, which is encountered in every problem related to the localization phenomena. So this is very important constant if you want to analyse or verify whether experimental phenomenon observed has localization nature.

Experimentally the weak localization effect has been observed and confirmed many times, especially in the metals. The given experiments performed on the Cu^{40} fully support all theoretical calculations that were proposed regarding the weak localization. At the temperature below 10 K, the evolution of the conductivity is different. The increase in the resistance $\Delta R/R$ is seen to be logarithmic, which agrees with equations.

Figure 1.5.2. Resistance vs Temperature for a Cu film with thickness $d=119 \text{ \AA}$ and resistivity $\rho_{4.2 K} = 6.8 \times 10^{-6} \Omega cm$ (Van den dries *et al*)⁴⁰

1.6 Magnetic effect on the quantum interference

In the presence of the external magnetic field trajectories of the conducting electrons will be affected, because moving electrons are bent by the magnetic field. Thus by applying the external magnetic field we should also provide another quantum correction to the electron conductance. Important contribution from the magnetic field to consider is the additional phase factor that electron acquires by travelling around the loop by the magnetic field. Of the impurities in the system will have their own contribution by scattering the electrons, which is given by $l/r = \Omega\tau$ as an order angle change due to scattering, where $\Omega = eB/mc$ is

cyclotron frequency. Generally for the dirty metal the scattering is not high, thus we can consider the case $\Omega\tau \ll 1$, so in our further analysis we'll ignore the contribution from scatterings. In the previous section we have analysed the probability of the electron to be found at the starting point by summing its electron wavefunctions. In our case we can find the probability of the electron by the same method, but here we have also additional phase for the electron wavefunctions.

$$\Psi \rightarrow \Psi \exp\left(i \frac{e}{\hbar c} \int \mathbf{A} d\mathbf{l}\right) = \Psi \exp\left(\pm \frac{i\pi BS}{\Psi_0}\right) \quad (1.6.1)$$

where $\mathbf{A}$ is the vector potential of the magnetic field, $BS = \Phi$ is the total magnetic flux through the electron loop, and $\Psi_0 = \pi\hbar c/e$ is a magnetic flux quantum. The area of the loop S could be roughly estimated to be circular with the radius r , more over we can also relate the area to the diffusion since $r^2 \simeq Dt$. For the weak localization we have considered two electron waves that travel around the loop and return to the origin point. In the Eq.1.6.1 the $\pm$ sign relates to the direction of the electron motion, so the two electron waves completing a loop in opposite direction will have phase difference. This phase difference of the electron wavefunctions is given by the

$$\varphi = 2\pi \left(\frac{\Phi}{\Phi_0}\right) = 2\pi \left(\frac{BS}{\Phi_0}\right) \simeq \frac{Br^2}{\Phi_0} \simeq \frac{BDt}{\Phi_0} \quad (1.6.2)$$

Similarly we can provide the equation analogous to the Eq.1.5.3

$$|A_1 + A_2|^2 = |A_1|^2 + |A_2|^2 + 2|A_1||A_2| \cos \varphi = 2A^2(1 + \cos \varphi) \quad (1.6.3)$$

If the $\varphi \rightarrow 0$ then our final result again will be $4A^2$. But for larger values of $\varphi > 1$ we need to consider the contribution coming from magnetic field to the quantum interference of the electron wavefunctions. In this situation the electron will acquire different phase angles by going through scattering events from the impurities. Then looking to the Eq.1.6.3 we have to calculate the average value of the term $\cos \varphi$, which is $\overline{\cos \varphi} = 0$. So the end result obtained will be same as classical value $2A^2$. The quantum interference has been destroyed by

magnetic field. The important parameters in the equation of φ are B and t . Meaning that the longer time the smaller magnetic field required to destroy quantum interference, and larger the magnetic field smaller time required. For the given constant magnetic field there is going to be particular time limit before all quantum interference can occur successfully. After this time limit the phase memory of the electron waves will be lost and the reason is magnetic field. The time constant τ_φ is different parameter, which comes from elastic scattering. Similar to the phase breaking time constant τ_φ we can also introduce magnetic phase breaking time

$$\tau_B = \frac{\Phi_0}{BD} \approx \frac{r_B^2}{D} \approx \Omega^{-1} (k_F l)^{-1} \quad (1.6.4)$$

where $r_B = (\hbar c / 2eB)^{1/2}$ is the magnetic length.

With the increasing magnetic field the magnetic time will be decreasing, which means that the quantum interference could be observed at lower time since $t < \tau_B$. With the use of the magnetic field we can manipulate the phase breaking time τ_B , thus this is an useful tool to confirm and analyse the weak localization in the disordered systems. Similar to the magnetic time we can introduce the parameter of magnetic field constant B_φ that will indicate the magnetic field exceeding which will break the phase memory of the electron wavefunctions. For this matter apply the condition $\varphi = 1$ for the Eq. 1.6.2

$$B_\varphi = \frac{\hbar c}{e} (D\tau_\varphi)^{-1} \quad (1.6.5)$$

Since under external magnetic field we have another time constant τ_B , the conductivity equations given by Eq. 1.5.8-1.5.10 may not hold always. Because for the condition $\tau_B < \tau_\varphi$ the integration limits must change, the final outcome is as follows

$$0 < \Delta\sigma(B) - \Delta\sigma(0) \approx \begin{cases} 2 \frac{e^2}{\hbar} \ln(L_\varphi / r_B), & d = 2 \\ \frac{e^2}{\hbar} \left[\frac{1}{r_B} - \frac{1}{L_\varphi} \right], & d = 3 \end{cases} \quad (l \ll r_B \leq L_\varphi) \quad (1.6.6)$$

where $\sigma(0)$ is the conductivity at zero magnetic field.

So far we have analysed the case of the electrons enclosing different area S under magnetic field. But the constant area S can be achieved experimentally if the non-conducting rod can be covered with the thin metal on the surface. Applied external magnetic field along the length of the rod will force the conducting electrons to circle around the metallic outer surface of the rod. In this case all electrons that covered the same number of loops will have the same phase factor from magnetic field. In this case we can avoid the destruction interference at the origin, but instead have an oscillating contribution with the period

$$\Delta B = \frac{\Phi_0}{S} = \frac{\pi \hbar c}{eS} \quad (1.6.7)$$

Of course it's necessary to have an area S , which is less than an phase breaking area L_φ^2 . Since magnetic field also introduces phase breaking, we cannot observe the quantum oscillations at high magnetic fields. These quantum interference oscillations are called as Aharonov-Bohm oscillations⁴¹.

FIG. 1.

Figure 1.6.2. Longitudinal magnetoresistance oscillations in cylindrical Mg films, solid lines show the experimental curves, the arrows indicate the calculated values of the field at which the resistivity extrema should be observed (Sharvin *et al.*)⁴²

1.7 The concept of spintronics and spin polarization

Recently, a new field called spin-electronics or “spintronics”,⁴³⁻⁴⁵ has grown dramatically. In traditional microelectronics, the charge is utilized but the spin of the electron is ignored. Scientists and engineers have created many devices based on conventional charge based electronics, such as field effect transistors (FETs), operational amplifiers, diodes, and read only memory (ROM). In spin based electronics (spintronics), both the electronic charge *and* the electron spin are utilized, providing new opportunities for a generation of devices combining standard microelectronics with spin-dependent effects that arise from the interaction between the spin of the charge carrier and the magnetic properties of the materials involved.

Adding the spin degree of freedom to conventional semiconductor charge-based electronics or using the spin degree of freedom alone could provide substantially more capability and performance to electronic products. For example, the magnetic random access memory (MRAM) is non-volatile, has no boot-up time and lower power consumption, which are the preferred properties for the memories in cell phones, digital cameras, and other portable electronic devices.

To realize further devices, we will need to manipulate electron spins on sufficiently fast time scales, transport spin-polarized carriers across relevant length scales and interfaces, detect spin coherence in nanostructures, optimize electron spin lifetime, and precisely control the coupling between electron spin and photons. The effort to merge electronics, photonics and magnetism could lead to new spin-based multifunctional devices, such as the spin-FET, spin-LED (light-emitting diode), spin-RTD (resonant tunnelling device), optical switches operating at terahertz frequency, modulators, encoders, and quantum bits for quantum computation and communication.

Figure 1.7.1 The schematic diagram of the band structure for a ferromagnetic metal.

A key component common to all spintronic devices is a source of spin polarized carriers, most commonly a ferromagnetic material. The schematic diagram of the band structure of a conventional metallic ferromagnet is shown in Fig.1.7.1, of which the Fermi level is located deep into the conduction band. Because of the exchange splitting in a ferromagnet, the electrons at the Fermi level in ferromagnets are spin polarized. It is clear that in many cases the performance of the spintronic devices is dramatically improved if this electron source is highly polarized, i.e. if the polarization of the electron spins at the Fermi level is large. In terms of the electronic band structure shown in Fig. 1.7.1, the spin polarization is usually defined by⁴⁶⁻⁴⁷

$$P_N = \frac{N_{\uparrow}(E_F) - N_{\downarrow}(E_F)}{N_{\uparrow}(E_F) + N_{\downarrow}(E_F)} \quad (1.7.1),$$

where $N_{\uparrow,\downarrow}(E_F)$ is the spin-dependent density of states at E_F . Spin polarized photoemission is a technique that is capable of providing such a direct measurement of P , but it suffers from poor energy resolution and extreme surface sensitivity. Alternatively, the spin polarization can be probed by electron tunnelling across an insulating barrier, either using two ferromagnetic electrodes or one ferromagnetic and one superconducting electrode. The tunneling spin polarization is defined by⁴⁶⁻⁴⁷,

$$P_T = \frac{N_{\uparrow}(E_F)|T_{\uparrow}|^2 - N_{\downarrow}(E_F)|T_{\downarrow}|^2}{N_{\uparrow}(E_F)|T_{\uparrow}|^2 + N_{\downarrow}(E_F)|T_{\downarrow}|^2} \quad (1.7.2),$$

where $T_{\uparrow,\downarrow}$ is the (potentially spin dependent) tunneling matrix. Point Contact Andreev Reflection (PCAR) in the ballistic transport regime can also be used to measure spin polarization, the relevant definition being⁴⁷

$$P_I = \frac{N_{\uparrow}(E_F)v_{F,\uparrow} - N_{\downarrow}(E_F)v_{F,\downarrow}}{N_{\uparrow}(E_F)v_{F,\uparrow} + N_{\downarrow}(E_F)v_{F,\downarrow}} \quad (1.7.3),$$

where v_F is the Fermi velocity. If the electronic transport in the Andreev reflection measurement is diffusive, then v_F is replaced with v_F^2 . It is therefore important to note that different definitions of spin polarization are accessed in different experimental situations.

1.8 Anisotropic magnetoresistance (AMR)

The resistivity in materials may depend on the relative orientation of the current density J and applied magnetic field, which is usually named as anisotropic magnetoresistance (AMR). If the current and applied magnetic field keep in the same plane of the sample, we called the resistivity variation as in-plane AMR. In-plane AMR is usually found in various ferromagnetic materials, such as ferromagnetic metals, magnetic semiconductors, and magnetoresistive oxide. Assuming $J = j_x \hat{x}$ and magnetization (M) are in the x - y plane with an angle $(\theta_{M,J})$ between the current and M . The generated electric field can be formulated as

$$E_x = \rho_{\perp} j_x + (\rho_{\parallel} - \rho_{\perp}) j_x \cos^2(\theta_{M,J}) \quad (1.8.1)$$

$$E_y = (\rho_{\parallel} - \rho_{\perp}) j_x \sin(\theta_{M,J}) \cos(\theta_{M,J}), \quad (1.8.2)$$

where $\rho_{\parallel}$ and $\rho_{\perp}$ are the resistivity with $\theta_{M,J} = 0^\circ$ and 90° , respectively. The in-plane AMR value is usually defined as

$$AMR = \frac{\rho_{\perp} - \rho_{\parallel}}{\rho_{\perp}}. \quad (1.8.3)$$

In ferromagnetic materials, the orientation of magnetization is determined by the direction and magnitude of the applied magnetic field and internal magnetic anisotropy of the

material system. Experimentally, it is more convenient to measure the variation of resistivity with the angle between the current and applied magnetic field ($\theta_{M,J}$). In ferromagnetic materials, in-plane AMR is due to the spin-orbit interaction and spin-polarized electron transport. It is a very useful tool for studying the underlying physical mechanisms of electron transport. McGuire and Potter predicted that the sign of AMR in ferromagnetic material is determined by the spin polarization of transport electrons. If a spin polarized material had a positive in-plane AMR ($\rho_{//} < \rho_{\perp}$), it would show a negative in-plane AMR if we can tune the spin polarization to the opposite sign. This theoretically predicted correlation between AMR and spin polarization has been experimentally confirmed in a ferromagnetic system with tunable spin-polarization, $\text{Co}_{1-x}\text{Fe}_x\text{S}_2$. Therefore, in-plane AMR can be used as strong experimental evidence of the existence of spin-polarized current. It has also been proposed to have potential application in spintronics. As the in-plane AMR can generate a voltage along y direction sweeping from positive to negative (Eq. 1.8.2), it can be used for designing logic and magnetic random access memory devices, where the absolute value of $\rho_{\perp} - \rho_{//}$ determines the sensitivity of the devices. Furthermore, the first electric gate tuned in-plane AMR has been discovered in dilute magnetic semiconductor (Ga, Mn)As, which offers new possibilities for attaining great improvements in performance over metallic devices.

References

1. E.H. Hall, *Am. J. Math.* **2**, 287 (1879)
2. L. D. Landau, *Z. Phys.* **64**, 629 (1930)
3. K. von Klitzing, G. Dorda, M. Pepper, *Phys. Rev. Lett.* **45**, 494 (1980)
4. D. Thouless, M. Kohmoto, M. Nightingale, M. den Nijs, *Phys. Rev. Lett.* **49**, 405, (1982)
5. J. Bellissard, A. van Elst, H. Schultz-Baldes, *J. Math. Phys.* **35**, 5373 (1994)
6. R. Laughlin, *Phys. Rev. B* **23**, 5632 (1981)
7. M. V. Berry, *Proc. R. Soc. London Ser. A* **392**, 45, (1984) 60
8. C.A. Mead and D.G. Truhlar, *J. Chem. Phys.* **70**, 2284–2296 (1979)
9. X. L. Qi, S.C. Zhang, *Physics Today* **63**, 1 (2010)
10. J. E. Moore and L. Balents: *Phys. Rev. B* **75**, 121306 (2007)
11. L. Fu, C. L. Kane, and E. J. Mele, *Phys. Rev. Lett.* **98**, 106803 (2007)
12. R. Roy, *Phys. Rev. B* **79**, 195322 (2009)
13. M. Konig, S. Wiedmann, C. Brune, A. Roth, H. Buhmann, L. Molenkamp, X.-L. Qi, and S. C. Zhang, *Science* **318**, 766 (2007)
14. D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, *Nature* **452**, 970 (2008)
15. H. J. Zhang, C. X. Liu, X. L. Qi, X. Dai, Z. Fang, and S. C. Zhang, *Nat. Phys.* **5**, 438 (2009)
16. C. X. Liu, X. L. Qi, H. Zhang, X. Dai, Z. Fang, and S. C. Zhang, *Phys. Rev. B* **82**, 045122 (2010)
17. Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, *Nat. Phys.* **5**, 398 (2009)
18. Y. Jiang, Y. Wang, M. Chen, Z. Li, C. Song, K. He, L. Wang, X. Chen, X. Ma, and Q. K. Xue, *Phys. Rev. Lett.* **108**, 016401 (2012)
19. D. Shoenberg, *Cambridge University Press* (1984)
20. L. D. Landau, E. M. Lifshitz, *Pergamon Press* (1977)
21. G. P. Mikitik and Yu. V. Sharlai, *Phys. Rev. Lett.* **82**, 2147 (1999)
22. Z. Ren, A. A. Taskin, S. Sasaki, K. Segawa, and Y. Ando, *Phys. Rev. B* **82**, 241306 (2010)
23. D.X. Qu, Y. S. Hor, J. Xiong, R. J. Cava, and N. P. Ong, *Science* **329**, 821 (2010)
24. A. A. Taskin, Z. Ren, S. Sasaki, K. Segawa, and Y. Ando, *Phys. Rev. Lett.* **107**, 016801 (2011)
25. J. G. Analytis, R. D. McDonald, S. C. Riggs, J. H. Chu, G. S. Boebinger, and I. R. Fisher, *Nat. Phys.* **10**, 960-964 (2010)
26. B. Sacepe, J. B. Oostinga, J. L. Li, A. Ubaldini, N. J. G. Couto, E. Giannini, and A. F. Morpurgo, *Nature Commun.* **2**, 575 (2011)
27. M. Lang, L. He, F. Xiu, X. Yu, J. Tang, Y. Wang, X. Kou, W. Jiang, A. V. Fedorov, and K. L. Wang, *ACS Nano* **6**, 295 (2012)
28. H. Cao, J. Tian, I. Miotkowski, T. Shen, J. Hu, S. Qiao, and Y. P. Chen, *Phys. Rev. Lett.* **108**, 216803 (2012)
29. L. He, F. Xiu, M. Teague, W. Jiang, Y. Fan, X. Kou, M. Lang, Y. Wang, G. Huang, N.-C. Yeh, and K. L. Wang, *Nano Lett.* **12**, 1486 (2012)
30. M. Veldhorst, M. Snelder, M. Hoek, T. Gang, X. L. Wang, V. K. Guduru, U. Zeitler, W. G. van der Wiel, A. A. Golubov, H. Hilgenkamp, and A. Brinkman, *Nat. Mater.* **11**, 417 (2012)
31. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, *Nature* **438**, 197 (2005)
32. Y. Zhang, Y. W. Tan, H. L. Stormer, and P. Kim, *Nature* **438**, 201 (2005)
33. J. Xiong, A. C. Petersen, D. Qu, R. J. Cava, and N. P. Ong, *Physica E* **44**, 917 (2012)
34. A. A. Taskin, K. Segawa, and Y. Ando, *Phys. Rev. B* **82**, 121302 (2010)

35. A. A. Taskin and Y. Ando, *Phys. Rev. B* **80**, 085303 (2009)
36. Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, *Nat. Phys.* **5**, 398 (2009)
37. Y. L. Chen, J. G. Analytis, J. H. Chu, Z. K. Liu, S. K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z.-X. Shen, *Science* **325**, 178 (2009)
38. D. Hsieh, Y. Xia, D. Qian, L. Wray, F. Meier, J. H. Dil, J. Osterwalder, L. Patthey, A. V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, *Phys. Rev. Lett.* **103**, 146401 (2009)
39. B. L. Altshuler, D. Khmel'nitzkii, A. I. Larkin, P. A. Lee, *Phys. Rev. B* **22**, 5142 (1980)
40. L. Van den dries, C. Van Haesendonck, and Y. Bruynseraede, *Phys. Rev. Lett.* **46**, 565–568 (1981)
41. Y. Aharonov, D. Bohm, *Phys. Rev.* **115**, 485–491 (1959)
42. Sharvin, D. Yu, and Sharvin, Yu. V. *JETP Lett.* **34**, 272–275 (1981).
43. I. Zutic, J. Fabian and S. Das Sarma, *Rev. of Modern Phys.* **76**, 323 (2004)
44. S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova and D. M. Treger, *Science* **294**, 1488 (2001)
45. J. F. Gregg, I. Petej, E. Jouguelet and C. Dennis, *Jour. of Phys. D-Applied Physics* **35**, 121 (2002)
46. I. I. Mazin, *Phys. Rev. Lett.* **83**, 1427 (1999)
47. R. J. Soulen, J. M. Byers, M. S. Osofsky, B. Nadgorny, T. Ambrose, S. F. Cheng, P. R. Broussard, C. T. Tanaka, J. Nowak, J. S. Moodera, A. Barry and J. M. D. Coey, *Science* **282**, 85 (1998)
48. C. Kane, J. Moore, *Physics World* (2011)
49. Y. Ando, *Journal of the Phys. Soc. of Japan* **82**, 102001 (2013)
50. S. Y. Chou, D. A. Antoniadis, H. I. Smith, *IEEE Trans. on Elect. Devices* **34**, 4 (1987)

Chapter 2. Experimental procedures

All fabrication and characterization techniques are described in this chapter. Firstly, we will introduce the methods used to obtain the high quality topological insulator samples. Our growth methods vary for nanowire structures and to the large flakes. To confirm the quality of our topological insulator samples we have performed several quality analysis experiments. Then fabrication steps used in our project will be described briefly. Finally the electrical measurement techniques used to obtain results will be presented.

2.1 CVD synthesis of the Ag_2Te nanoribbons

Nanowires are one-dimensional (1D) nanostructures with diameters in the range of hundreds or less nanometers. Due to their unique geometry combined with nanoscale size they've provided physical phenomena different from bulk materials. For example, the nanowires synthesized from the same compounds but at different growth directions could successfully provide unique anisotropy features. And these 1D structures contain large surface to volume ratio and great mechanical flexibility.

It's highly important to control the growth direction of the nanowires, because of the anisotropy in some crystals. Thus the task of nanowire growth is to induce the 1D growth with controllable parameters. There are several techniques used in the fabricating of the nanowire structures, like chemical vapour deposition (CVD) mechanism, molecular beam epitaxy (MBE), and laser – assisted growth. But among all these methods the CVD growth mechanism is the most widely used method. This is generally due to the simplicity, versatility of the system, while some systems like MBE could consume more time and come costly to sustain.¹

Chemical vapour deposition (CVD) also offers several advantages like good film uniformity, compatibility, conformal growth, and high deposition rate. It's deposition of various solid materials using thermally induced reaction of molecules on heated surface. In our research work we are going to use standard CVD method for the synthesis of the Ag₂Te nanoribbons inside a 30 cm horizontal tube furnace equipped with a 3 cm diameter quartz tube (Fig. 2.1.1). Although the quality of the grown Ag₂Te nanoribbons might not be of high quality that could be achieved with the systems like MBE, the Ag₂Te samples obtained from this sample are found to be good quality samples that can be confirmed by the TEM analysis, which is given in the later chapters. But of course the growth procedures must be carried out carefully to preserve the sample qualities as desired, because slight changes in the growth parameters can easily give different structures other than nanowires. Purely chemical synthesis of the Ag₂Te nanowires doesn't match our desired standards of the sample quality, so we abandoned this idea. Another advantage of the CVD growth method is the adequate time consumption by the whole procedure; also it's easy to handle whole system. In general most of the nanowire growth using the vapour – liquid – solid (VLS) mechanism utilizes the catalyst, like Au or Ag, but the quality of the samples obtained by that method is lower. This method was introduced by Wagner in 1964 in Si industry². Since the catalyst is the main aspect of the nanowire growth in this method, the growth direction of the 1D structure can come out to be different in the same batch. But if the lattice constant of the substrate and the desired nanowire match, then it's possible to harvest the nanowire growth on this particular substrate with desired nanowire growth direction. In this way the quality of the samples can be increased considerably.

Before the growth the system is pumped down to the base pressure 3×10^{-7} torr to eliminate remaining oxygen and contamination inside a tube. The powder of Ag₂Te (Sigma-Aldrich, 99.99%) is used as a precursor placed at the hot center region. Sapphire substrates

are placed downstream 14-17 cm away from the hot center region without any catalyst. They are placed near the edge of the furnace, since in our horizontal quartz tube furnace the temperature gradient doesn't change significantly with the inside area. Thus the edge of the furnace is the region, where the temperature starts to drop dramatically considering that we've employed fans to cool the quartz tube regions outside of the furnace. So the source particles evaporated into the vapour droplets will start to condensate and deposit near the edge of furnace, where we have put our substrates. Importantly one should consider the stability of the quartz tube during the growth period or before. The slight fluctuations within the quartz tube could easily shift the light substrates from desired location, which in the end will give different nanostructures grown on the substrates. Especially the rough pump connected to the quartz tube, intended to keep the pressure inside stable, is going to contribute large portion of the quartz tube shaking. In this regard, we have separated the rough pump to the location further from the VLS growth area, while applying the buffers for the quartz tube to reduce shaking.

For our nanowire growth we have reused regularly the substrates and quartz tube. Preparing new sapphire substrate and quartz tube for every growth could be quite costly, as we have been growing nanowire samples about twice a week. The cleaning procedure is utilized for the cleaning of the sapphire substrates that are reused for the next growth. Generally the fresh substrates host epitaxial structures while reused substrates can give rise to standing nanostructures. Here are the steps for the cleaning of the sapphire substrates

1. The acid we have used for our cleaning is aqua regia, $\text{HCl} : \text{HNO}_3 = 3 : 1^3$. The given acid is highly corrosive against the metals and it's one of the traditional solutions often used in the laboratories for cleaning metallic contamination. The same mixture has been utilized in many of our cleaning procedures that will be mentioned later. The

sapphire substrates were placed into this mixture for 5 minutes, which is enough to destroy all Ag_2Te traces on the surface of the substrate.

2. Since our acid cleaning of the sapphire substrates mainly targets the metallic contamination inside the tube, we have been looking for the methods of cleaning the organic contaminations. Our first try-outs of RCA cleaning, named after Radio Corporation of America where it was developed, on the sapphire substrates turned out to be successful, and then we continued to employ this method for the quartz tube as well. RCA cleaning is a standard cleaning method used in the semiconductor industry. The main benefit we were looking from the RCA cleaning is the organic removal, but we have decided to utilize another step, which is called ionic contamination removal, to further improve our cleaning technique. In total there are three steps in the RCA cleaning: organic clean, oxide strip and ionic clean⁴. Obviously we don't require oxide strip step for the cleaning of quartz tube and sapphire substrates.

- a. Organic clean in the RCA cleaning is intended to get rid of the organic contamination. The solution of NH_4OH (ammonium hydroxide): H_2O_2 (hydrogen peroxide): H_2O (DI water) = 1: 1: 5 is prepared at the temperature 80°C . This solution is used to clean the sapphire substrates for about 10 minutes. Usually the glassware with the mixture is heated up to desired temperature and substrates are placed inside.

- b. Next step of cleaning is ionic clean, designed to remove ionic contamination. For this step another solution is mixed, HCl (hydrochloric acid): H_2O_2 : H_2O = 1: 1: 6 at temperature 80°C . Similarly the substrates are cleaned about 10 minutes.

3. After the RCA cleaning is performed on the sapphire substrates we need to flush it thoroughly using acetone and isopropyl alcohol (IPA). Inside these solutions our substrates are ultrasonicated for 15 minutes each. It's standard cleaning technique in most of the laboratories. After sonication the substrates are blown using nitrogen gas (N_2), then directly placed into the quartz tube and sealed. The importance of the surface cleanliness of the sapphire substrates is high. We don't employ the catalyst for the growth of the nanowire, because of that the vapour droplets require clean substrate surface to start the 1D growth. Too much dirt on the surface will definitely block the vapour droplets from the source from attempts to make any bonds with the sapphire.

The quartz tube cleaning can be very tricky, due to the fragility and the structures of the tube. For this matter, we have utilized similar cleaning procedure as described for the sapphire substrates, periodically using a long brush to make sure that every part of the tube gets cleaned. Before the growth, the tube is cleaned with acid to get rid of the remaining Ag_2Te traces and other metallic contamination. In the next step we utilize standard RCA cleaning methods to get rid of the organic and ionic contamination from the surface, but oxide strip step is skipped. Later quartz tube is further cleaned with acetone and IPA, and subsequently blown by N_2 gas. Even despite the described previous steps of the cleaning some contaminations have shown to be immune. Then the last step of our cleaning has been to heat up the quartz tube as high as $1000^\circ C$, which is slightly higher than the growth temperature. The system was kept at this temperature for about 3 hours and continuously pumped down. This technique is efficient to remove most of the contamination left after first 3 steps. If the contamination after these cleaning procedures is still significant and can't be removed, then it's wise to use new quartz substrate. Even for effective cleaning after many

growth procedures the contamination inside will accumulate, which suggests changing quartz tube from time to time.

After all necessary cleaning procedures are performed we can start the growth of the nanowires. The tube is flushed three times with the argon gas to decrease oxygen contamination. The typical growth conditions for the nanoribbons are: 0.026g Ag_2Te , pressure 7.5 torr, source temperature 980°C , growth time 1 hour, and gas flow rate 50 s.c.c.m. Nanoribbons generally grow at the position range of 15-16 cm away from the center. As grown ribbons are typically 100-200 nm thick, 100 nm to several micrometers wide, and up to tens of micrometers long.

Figure 2.1.1 CVD growth setup with the quartz tube installed to the furnace. As the source Ag_2Te located at the center of the tube is heated to the temperature 980°C , Argon gas carries the evaporation from the source downstream where sapphire substrates are located.

We generally have heated up the system slowly at 6°C per minute, which increases the lifetime of the furnace and stable growth of the surface of the substrates. While the system was ramping up from the room temperature to the growth temperature, we have continuously supplied the Argon gas to the system. In this way, we can control the system pressure more precisely and provide better condition to start growth. Because actual source evaporation starts at temperature lower than 980°C and largely affects the pressure within the system. One of the important parameters in our growth is the argon gas flow rate. The temperature

980° C is set to induce the evaporation of the source Ag_2Te , which melts the source into the liquid form to supply vapour droplets. If during the growth the source is fully evaporated, then it's required to reduce the temperature since it is evaporating the source too quickly. Thus when tuning the growth conditions it's better to fix temperature and change gas flow rate, instead fixing flow rate and changing temperature. Using flow rate we can tune the speed of the nanowire growth.

Figure 2.1.2. CVD grown Ag_2Te nanowires and nanoribbons under SEM.

So when the temperature reaches 980° C the Ag_2Te source starts to melt and evaporate. The argon gas input to the system will pick the evaporated Ag_2Te droplets and carry them along the tube to outlet, where the rough pump continuously supporting the pressure level of the system. But at the edge of the furnace these vapour droplets will experience the drop in the temperature and condensate to the sapphire substrates placed at that location. The Ag_2Te

vapour components will adsorb to the surface of the sapphire and form a chemical bond following the crystal structure of the sapphire. The argon gas flowing in the system is set to supply the source molecules to the designed substrate surface. The condition of pressure and gas flow rate will influence the rate of deposition of Ag_2Te molecules on the surface of substrate. If the argon gas flow rate is too slow, then vapour components will have enough time to drive around and achieve minimum free energy of the alloy system. In this case we are more likely to observe the epitaxial growth on the substrate. While faster gas flow rate will promote the 1D growth of standing nanowires. It's very important to control the flow rate and pressure of the system, especially the pressure will fluctuate during the growth due to evaporation from the source. Generally the nanowire growth occurred within the region 3-5 cm, so it's better to have substrate longer than that and cover the whole growth region. After the growth process is finished the furnace was left to cool down naturally with argon gas flowing continuously and rough pump pumping. These steps are to make sure that no oxidization would occur during the cooling down process, which usually takes place overnight. The next day sapphire substrate is taken out of the CVD system while nanowires are mechanically sonicated into the IPA solution, where they are kept until device fabrication.

Figure 2.1.3. Principle of CVD process (Palisaitis *et al.*)²¹

2.2 Material characterization

In this section we are going to describe the experimental tools and techniques used for the material characterization of our samples. Mainly the instruments that were used frequently are atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The characterization using TEM was done with the help of Zhang S. Y. from prof. Han M. Y. group from Institute of Materials Research and Engineering (IMRE), NUS.

2.2.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is one of the most useful tools in the material characterization. As can be seen in the name it uses electrons for the imaging instead of light like common optical microscopes. Since the developing of SEM machines they've shown many advantages over traditional microscopes. In our projects the SEM tool was used

importantly to study the elemental composition of the nanowires fabricated using CVD method. Depending on the parameters of growth conditions the composition of Ag_2Te can change easily, so according to the ratio obtained in SEM, we can further tune the growth conditions of CVD. Also we used SEM generally for imaging, analysis of structural growth tendencies. Further we can learn precisely the size of the nanowires fabricated in our furnace, for some measurements we have required certain sizes of nanowires.

The magnification in SEM can go as high as 500, 000 times the size of the object, which is known as magnification power, while the optical microscopes can achieve only few hundred times magnification. These large magnifications are achieved using electromagnets instead of lenses, thus better control could be obtained for the magnification. SEM also provides large depth of field, where the images are presented almost in 3D, which more convenient for researchers to analyse. The optical microscope can only generate flat 2D image. Also the resolution achieved in SEM is much higher than in traditional microscopes, so the closely located points in the specimen can be magnified at higher levels. Lastly, the SEM can provide the information about the composition of the material being studied. All these advantages make SEM imaging as important tool for research and material characterization.⁸

The essential parts of the SEM machine are as follows:

- Electron gun
- Magnetic lenses
- Scanning coils
- Vacuum chamber
- Sample stage
- Detectors

Electron gun is a part, where the electrons are generated. There are two types of electron guns: thermionic gun and field emission gun. The principle of the thermionic gun is rather simple; it applies the thermal energy into the tungsten filament. The heated filament starts to release electron gas into the system. The tungsten is the most commonly used material for the filament, because it has high melting temperature, low vapour pressure, and relatively cheap. The electrons in the field emission gun, as the name tells us, are created using very strong electrical field, which separates the electrons from atoms.

The magnetic lenses used in the SEM have the different purpose compared to optical lenses. Here they are supposed to focus the electron beam to a spot, while optical lenses are responsible for imaging. Meaning that the SEM can also function without the magnetic lenses, given the electron beam from electron gun sufficiently narrow, but the resolution for final image is not going to be good as with lenses. These lenses are made of magnets and able to bend, manipulate the direction of the electron beam. They are required to collimate, focus and scan the electron beam across the sample. The first magnetic lens in the path of electric beam is condenser lens. Electrons coming from the electron gun will be scattering in all directions, thus the condenser lens collects and condenses these electrons to create uniform beam of electrons. Generally the SEM machines have one or two condenser lenses. Then electrons are directed into desired direction by using scanning coils or pair of deflector plates. The electron beam can be scanned in the x and y direction over the sample to obtain all necessary information.

The primary electron beam is incident of the surface of the sample and electrons from the beam will interact with the surface of the specimen. The results of these interactions are generally will be the inelastic or elastic scattering, absorption of the electrons from the beam, secondary electron emission, and electromagnetic radiation. SEM detectors primarily focus on the collection of the secondary electrons, backscattered electrons, and x-ray radiation. Of

course, there are vacuum requirements for the SEM, since the collection of aforementioned electrons and radiation is sensitive. If the chamber would contain air molecules, they would interfere with the electron beam and as well with scattered electrons. Thus the final image will be significantly distorted.

The images provided by the SEM generally black and white due to the configuration of the machine, since there isn't enough information collected per pixel on the image and no information obtained about the actual color of the sample. Some SEM features can provide the colourful image for the sample imaging. They use several detectors that collect scattered electrons, analysing the properties of the secondary electrons and backscattered electrons, these detectors can identify some differences on the sample surface, like density, and assign different colours to these different features.

The emission of the secondary electrons after the inelastic scattering interaction with electron beam electrons is coming from the outer *k*-shell of the specimen atoms. Typically they have very low energy (< 50 eV) and exist only near the sample surface⁵. Frequently SEM machines use Everhart – Thornley detector⁶ for detection of secondary electrons, which is based on scintillator – photomultiplier system. The detector applied low voltage to attract the secondary electrons towards the detector. The low voltage is not sufficient enough to distract electrons from primary electron beam. Collected secondary electrons then accelerated by scintillator voltage (2, 000 V). These accelerated electrons will carry sufficient energy to cause the scintillator to emit photons. Later photons are directed towards the photomultiplier, which converts the incident light into electric current and amplifies the signal. Depending how strong the final signal the system will provide subsequent brightness to the image of this signal.

Figure 2.2.1. Principle of Scanning Electron Microscopy. (Diagram courtesy of Iowa State University)

Subsequent information about the material under characterization could be obtained from backscattered electrons. These electrons originate from the primary electron beam, after the interaction with the surface of sample these electrons are scattered elastically. Compared to secondary electrons the backscattered electrons are highly energetic. Theoretically the heavier atoms would scatter incident electrons stronger than the lighter atoms. So the detectors can distinguish the different chemical compositions that caused the elastic scattering of the electron. Usually the detectors are located just above the sample in the shape of a circle with a hole for electron beam to pass. Since the backscattered electrons will be

travelling in different directions this kind design of detectors allows them to capture as much as possible electrons. Usually the detectors for backscattered electrons are scintillator or semiconductor type.

Another interesting feature of the SEM machines is the energy – dispersive X-ray spectroscopy (EDS)⁷. This feature is used for the chemical characterization of the specimen. The primary electron beam incident on the surface of the sample produces also X-rays, as mentioned before. When the highly energetic electrons hit the sample some electrons from inner shell within the atomic structure of the sample absorb energy and break the bonds leaving a hole behind. Then electron from outer shell can drop to the lower energy level, the difference in energy levels is excited as X-ray photon. Every element has its own unique atomic structure, which will release different kind of X-ray radiation. The X-ray spectrometer in the EDS will analyse the energy and intensity of the signal detected. The subsequent information can tell us about the elemental composition of the sample under characterization.

2.2.2 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a high resolution scanning probe microscopy. It's one of the essential tools in nanoscale for imaging, measuring different subjects like height, magnetism, etc. The probe of the AFM is a sharp tip of cantilever, generally made of silicon or silicon nitride. Ideally the tip should narrow down as low as few atoms at the end of it for high sensitivity. When the probe is driven close to the surface, the atoms at the tip will interact with the surface atoms. This interaction will lead to either attraction or repulsion of the tip that will cause the deflection of the cantilever. Analysing the mechanical deflection of the cantilever we can measure different kind forces, like magnetic force, chemical bonding, van der Waals force, and etc. The laser located about the cantilever ejects a laser beam towards the cantilever. Depending on the deflection of cantilever the laser beam is reflected

differently, this reflection is collected by photodiodes and further processed for imaging of the sample.⁹

The measurements in the AFM must be carried out carefully, because the tip of the cantilever can be damaged easily. Most common usage of the AFM tool is the profile measurement of the sample. If during the scanning on the plane of sample the tip encounters some height, then it can contact the sample and get damaged. Usually the small piezoelectric crystals are implemented to the cantilever. These crystals allow the tip to scan in x , y and z direction more accurately, abstaining from collision with surface of specimen.

There two main scanning modes for the AFM machines: contact mode and tapping mode. For the contact mode the force between tip and surface is kept constant. So the tip will scan the surface of the sample with constant distance between tip and surface, when there is change in profile within the sample the tip deflection will sense any changes and slowly adjust to new profile. The tapping mode involves the oscillation of the cantilever instead of keeping it steady. Here the cantilever oscillates at near its resonance frequency, which is caused by another piezoelectric crystal implemented to the cantilever. The amplitude of the oscillations is generally 100 to 200 nm. The changing the profile of the sample surface will give different interaction of the tip with surface, thus it will affect the oscillation amplitude as well. This change in amplitude is detected by the machine and information about the specimen is extracted. This method is safer than the contact mode, because it doesn't involve continuous interaction of surface with tip.¹⁰

For our research the AFM machine was used mainly for the measurement of nanowire thicknesses. Since we can use SEM to measure the width of the nanowires, it's practically impossible to measure the thickness, even if the sample holder could rotate along x , y and z still the task will be too tricky. The AFM in fact can measure the width of nanowires as well

since it's scanning along the surface, but the information regarding the width is inaccurate due to low resolution coming from scanning modes.

Figure 2.2.2. Principle Atomic Force Microscopy. (Diagram courtesy of Nanoscale Informal Science Education)

2.2.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is another microscopy that's similar to the SEM and also involves electron in obtaining the imaging. Thus this is another electron microscopy that allows detailed examination of the sample with high resolution and high magnification imaging. But difference for TEM is that the electrons are transmitted through the specimen instead of scanning through the surface. This allows obtaining the morphological, crystallographic, as well as compositional structure of the sample.

In fact the TEM machine was designed earlier than the SEM and it was the first microscopy that involved electrons for imaging. Because the light photons have certain

wavelength, it was the major problem in the development of the microscopy as it was limiting the higher resolution of the optical microscopes. Even though electrons also behave like a wave, they carry very small de Broglie wavelength. The first design of electron microscopy was provided by Ernst Ruska and Max Knoll in the early 1930s¹¹. They also constructed the first electron microscopy during the same time. The new microscopes based on electron imaging quickly surpassed the resolution and magnification of the optical microscopes.

The structure of the TEM machine is similar to the SEM we have described earlier. The electron gun also consists of either thermionic gun or field emission gun. Thus electrons are created from the filaments by the means of applied high voltage. The electron gun has a hole, which allows electrons only for certain angle to escape through it and contribute for the imaging. The primary electron beam then collimated by the magnetic lenses. Since the electron beam from the electron gun will be diverging, the first in their path will be the condenser. The purpose of the condenser is to collimate the given electron beam. These magnetic lenses usually made of iron, iron-cobalt or nickel-cobalt alloys. The magnetic lenses must be calibrated very accurately, because any non-symmetry will cause aberrations of the electron beams.

Figure 2.2.3. Principle of Transmission Electron Microscopy. (Muller)²²

The electron beam is later transmitted through the sample and final image is projected on the back screen. Due to the absorption of the electrons by the specimen, it's required for the TEM to prepare the sample as thin as possible, generally $< 50\text{nm}$. The transmitted electrons would commonly provide images with low contrast, because interaction with sample will give directly transmitted and diffracted electrons. It's possible to insert diaphragm at the back focal point to select only transmitted electrons. In this case the image will be obtained in the *bright field* mode, where all amorphous, not Bragg oriented crystalline parts will be shown as bright, while Bragg orientation will be dark. Generally thicker parts of the sample will tend to diffract the electron beam strongly, as well as heavy atoms will affect electrons more. In the similar way the image can be provided using the diffracted electrons,

to do this the beam is slightly tilted and diaphragm for this condition will select only diffracted electrons. This is called *dark field* mode.¹²

Figure 2.2.4. Bright and dark field modes for imaging.²³

2.3 UV Photolithography

Photolithography refers to the process of obtaining desired geometric patterns on the substrate, like silicon wafers. It usually involves the deep ultra violet (UV) light source to expose certain areas of the light sensitive photoresist coated on the sample. It's a frequently used tool in the microfabrication of the semiconductor circuits. Nowadays the construction of the transistor requires a lot of the complex structures in the microscale. It provides a lot of advantages for the semiconductor industry, like the ability to create patterns over large surfaces that will decrease the cost, small time consumption, precise control over the pattern size and shape. One of the drawbacks of using the UV photolithography is that it requires a flat substrate, thus the direct beam from the machine will create flat shapes on the photoresist. The manufacturer needs to implement more advanced techniques during the deposition or etching in order to generate non-flat structures on the substrate. Generally the

photolithography machines can create structures as small as few hundred nanometers, which suits for many purposes of the device fabrication, though the smaller structures must be fabricated using electron beam lithography (EBL), which is extremely time consuming and costly to maintain. Modern integrated circuits (IC) manufacturing requires as many as 50 steps of lithography patterning. As we mentioned UVL and EBL have their own advantages and disadvantages, and their limits also limit the progress of the IC.

The UV photolithography as already mentioned employs the photoresist, light sensitive polymer. This photoresist is exposed to the UV light and developed leaving the desired pattern on top of the substrate. The pattern obtained on the photoresist must be ideally just like the pattern on the photomask with vertical walls, but of course due to the properties of light waves we'll observe some differences. Generally the UV photolithography consist of these main steps

- Substrate preparation
- Photoresist coating
- Prebake
- Align and expose
- Post exposure bake
- Second exposure
- Developing
- Material deposition
- Resist strip

In the following chapters we'll briefly describe all these steps in the UV photolithography.

Figure 2.3.1. Photolithography process with photoresist utilized as negative photoresist. There are two exposure steps with no photomask applied in the final exposure. All non-exposed area in the initial exposure will become soluble after the final exposure. Later metal contacts are deposited using Sputtering method and lifted-off leaving only designed pattern on the surface of the substrate.

2.3.1 Substrate preparation

The substrate preparation is one of the crucial steps in obtaining the photoresist pattern as good as possible. Another disadvantage of the UV photolithography is the requirement of clean manufacturing area. The typical photoresist thickness is in the range of 1-2 μm , thus any contamination within the size of micrometers can significantly affect photolithography manufacturing. It's in the best interest to keep substrate as clean as possible. Generally used silicon substrates can be cleaned chemically using IPA, acetone, and methanol. In the case of the strong organic contamination the RCA cleaning method must be applied. To get rid of the water from the substrate the heating procedure is also can be done. During our experiments we have tried to use new silicon wafer for every device fabrication, this method decreases the contamination considerably. The new silicon substrates were cut into the $\sim 2 \times 2 \text{ cm}^2$ pieces

using the diamond cutter. Next step is ultrasonication in acetone (15 mins) and IPA (15 mins). The order of these solutions is come out to be important for our fabrication. Acetone is more aggressive than IPA in the cleaning, but it's more volatile as well. Initially only acetone was used for ultrasonication, but when we took out substrates from acetone, the later solution evaporated too quickly leaving some dry dirt behind. The extra step with IPA is to solve this problem, so in the end we can blow substrates with nitrogen gas.

When the substrate cleanliness is achieved, then we can proceed to transfer the sample to the silicon substrate. In our projects the sample was Ag_2Te nanowires and Bi_2SbTeSe thin films. The nanowires were stored inside the IPA solution, and then transferred to the SiO_2 substrate using micropipettes. Even though we made sure that our substrate was clean larger amount of contamination actually comes from the IPA solution to where we have ultrasonicated freshly grown nanowires. To solve this problem we have diluted the nanowire solution, but made sure we still have enough nanowires otherwise finding desired nanowires will be difficult. Generally we have dripped about 1-2 μl of IPA-nanowire solution onto the $\sim 2 \times 2 \text{ cm}^2$ 300nm p-type SiO_2 substrate. If we can at least one good nanowire after dripping it will be more than enough, because photolithography doesn't allow patterning two devices at the same time on the same substrate.

With dilute solution we also decreased the concentration of the dirt. In the case of existence of contamination on substrate one needs to make sure that it's far enough from the actual area of patterning. Like in our project we have tried to pick nanowires that stay far from dirt, that dirt can be actually removed by hand in some cases. But in this rough method we need to be careful not to damage the nanowire. Before the dripping of the nanowire-IPA solution it's better to ultrasonicate it for 1-2 minutes, because the nanowires tend to condense within the solution. Even though the solution must be used in the first 2-3 weeks after the growth, after that nanowires cannot be found easily or entangle with each other. Also the

larger size of the substrate will host more non-uniformities and dirt, thus this will take its toll on the final lithography pattern. Too small substrate will consume more time for searching nanowire structures after dripping, also the nanowire sample too close to the edge can't be used for photolithography because at the edge the patterned device contacts will be cut short or touch bottom silicon. So depending on the device being manufactured one has to consider optimal size of the substrate. Dripping so small amount of IPA like 1-2 μl is also important for the photoresist. After the dripping, the substrate was left to dry in the air, some dirt within the solution will absorb and preserve IPA liquid through this process. The more IPA you drip the more dirt and more IPA liquid will be left on the surface of substrate. In the latter developing process, the photoresist will reach with these IPA contained dirt, since photoresist can be destroyed by alcohol solutions, the pattern obtained on photoresist will be dramatically distorted.

For Bi_2SbTeSe we have used the mechanical exfoliation to transfer this material onto the SiO_2 substrate. For the materials that are composed of stacked layers of atoms the mechanical exfoliation can be performed successfully. The substrate picked for the fabrication of the devices was always 300 nm p-type SiO_2 . The main reason was the voltage gating tunability of the substrate, but also another important advantage of this substrate is the clear contrast image of the samples through the optical microscope. The exfoliation is performed using a scotch tape. The tape is applied on the bulk piece of Bi_2SbTeSe and slowly removed, peeling away thick and shiny layers of Bi_2SbTeSe . Then peeled Bi_2SbTeSe is again refolded upon clean section of the same piece of tape. This process is repeated several times until the thickness of the Bi_2SbTeSe decreased sufficiently. Generally the shiny layers will become more grey-like. When this condition achieved the tape is applied gently upon the clean SiO_2 substrate. We have used rubber to apply the tape on SiO_2 uniformly, without leaving any air bubbles. One shouldn't press down the tape too strongly, sticking the tape to substrate even

more. In general the tapes with lower adhesion are preferred, as well as those which don't leave much contamination on substrate. After few minutes the tape can be removed from the substrate. The clean SiO_2 surface doesn't stick to the tape strongly, so removing tape must be going easily. If the tape stuck to the SiO_2 too strongly, that means that substrate wasn't cleaned well enough. This substrate can't be used for further device fabrication, because it will contain too much tape and Bi_2SbTeSe left-overs.

2.3.2 Photoresist coating

For the photoresist coating there are spin coaters designed to perform this task. The spin coater sucks substrate with sample into the stage by using a vacuum, to make sure that substrate will stay firm during spinning. This is widely used technique in the microelectronics manufacturing, because it provides good resist homogeneity and small time consumption. In this step of photolithography the photoresist is transferred upon the substrate using pipette. Few ml of photoresist is generally enough to coat whole surface of the substrate, unless your substrate is too large. Then the spin coater accelerates the substrates into the spinning with several 1, 000 rounds per minute (rpm). The speed and time of spin coating must be chosen appropriately to achieve the uniform distribution of the photoresist throughout the surface. But the main disadvantage of the photoresist coating is the edge beads generated during the coating due to air turbulences. The edge beads will have higher thickness than intended for the photoresist thin film. Later in the mask alignment sometimes in order to achieve exposure as good as possible we have to get mask and substrate as close as possible. But the edge beads will always prevent decreasing the gap between substrate and mask.¹³

We haven't analysed how much the acceleration speed affects the homogeneity of the photoresist, because generally it takes within a second to reach highest rotation speed and small changes we have made didn't affect our end result. Depending on the photoresist type

the thickness of the resist film can vary, because different photoresist have different densities, viscosities. By changing photoresists we can obtain different properties for the photoresist thin film. Mainly we consider the thickness of the resist, which is crucial in later steps like developing and resist stripping. Generally the thickness of the photoresist for the particular photoresist, rotation speed, and time can be obtained from the manufacturer. Also measurement of resist thickness can be done generally using optical methods, such as transmission or reflection spectroscopy.

Some important considerations must be taken when pouring photoresist upon the substrate. First of all the photoresist itself must be stored properly, no contamination must be allowed to mix with the liquid. Every time before spin coating one must check whether visible dirt, bulk particles can be found in the resist. The pipette for the spin coating shouldn't be reused, unless it's cleaned properly. Secondly, when dispensing the photoresist liquid upon the substrate we have to make sure that no air bubble is formed. These air bubbles will also contribute to morphological irregularities on resist film.

After the spin coating the substrate should be analysed with naked eyes on sight. The photoresist thin film must be uniform looking; the dirt within the size range of micrometres will be easily visible since the photoresist thickness is 1-2 μm . In this case it's better to wash the substrate with acetone that will dissolve resist, and apply the photoresist again. Some abrupt irregularities within the photoresist also can be noticed, because the color of the photoresist will change with the thickness change due to diffraction.

2.3.3 Prebake

Next step after the spin coating of the photoresist is called prebake, or softbake. This step is necessary to dry out the resist, since it's coming from liquid solution. Depending on the photoresist type the solvent concentration remaining will vary, thus different baking time

must be applied to the photoresist. There different purposes of the prebake process, but in this paragraph I'll describe the essential issues involved in our photolithography fabrications.

The photoresist must be bakes sufficient enough to make it hard. In the following step we'll perform the mask alignment and UV exposure. As I've already mentioned before the gap between photomask and photoresist must be kept as small as possible during UV exposure. The remaining liquid within the photoresist can easily promote sticking of the photoresist and photomask. This complicates our mask alignment significantly, because the substrate can't be moved to the desired location when stuck to the photomask. Also it contaminates the photomask, thus during the UV exposure this contamination will block UV light passing through the photomask. Some contaminations turned out to be very difficult to remove, which can later make photomask unusable.

There is N_2 -release in the photoresist during UV exposure, because the photo active compound (PAC) in the resist converts into carboxylic acid separating N_2 molecule. This nitrogen gas will diffuse through the resin towards the surface of the photoresist. For the insufficiently baked photoresist the N_2 gas will cause bubbling on the surface, which is visible by the eyes as milky appearance. In this case prebake process must be reconsidered again.¹⁴

2.3.4 Align and expose

The basic principle of the UV exposure process is to change the solubility of the exposed photoresist. There are generally three types of photoresist: positive, negative and image reversal photoresists. Depending on the device being fabricated the manufacturer can chose photoresist of their preference, since every resist presents its own advantages.

The positive photoresist contains photo active compound (PAC), which is generally diazonaphthoquinone (DNQ)¹⁵. This compound is not soluble in the developer solution, but the UV light in the range of 350-450 nm converts it into the carboxylic acid. The carboxylic acid can be actively dissolved in the base developer solution. So by exposing certain areas of the photoresist we can later dissolve them in the developer, which will give us desired pattern on the substrate. The negative photoresist works opposite to the positive, meaning that the developer is going to develop unexposed areas instead of exposed. Typically negative photoresist contains certain PAC, and UV exposure will destroy bonds of this compound. Post exposure hard baking will promote cross-linking of these broken bonds with the resin, which finally converts the exposed areas into insoluble resist. The image reversal photoresist is the mix of positive and negative photoresist. It can be used just like the positive photoresist, so after first exposure the exposed areas can be developed. But post exposure baking also will make exposed areas insoluble. After postbake the whole photoresist must be exposed to UV light again. The cross-linked areas are not going to suffer from second exposure, while unexposed parts from first exposure now will become soluble.

The advantages that photoresists offer generally concerns lift-off, mask aligning, substrate adhesion. I'll discuss the lift-off process in later chapters. The negative photoresist provides better adhesion to various types of substrates, like Si, GaAs, InP, metals, and glass. But the available positive photoresists in the market are much easier to strip.

In the photolithography microfabrication process the most difficult part is the mask aligning. This process is performed mainly by hand using an optical microscope. The light in the microscope is provided by a fluorescent lamp with specific filter to capture UV components. This light appears in the yellow color and it's not pleasing for the user in terms of brightness. Generally photolithography machines don't provide high magnification power

that can expose photoresist during alignment. For our fabrication SUSS MicroTec MJB4 Mask Aligner system had maximum 20x magnification power.

Typically the mask alignment consists of three methods: contact, proximity and projecting exposures. Contact exposure requires contact between photomask and sample, thus the gap between them must be closed. This allows high resolution printing on the photoresist. But this method might be too rough for the photomask, especially if the chromium pattern on the photomask is not of good quality, also it contaminates the photomask. In the proximity exposure there is gap between photomask and sample. This method is preferred if the pattern to be printed is of large sizes. In our fabrication we needed patterns as small as 1-2 μm , which requires us to use contact exposure. There is also projection exposure, which is mainly used in the industry. In this method the optical lenses controlled by computer project the UV light to the sample. Thus this method provides good resolution as in contact exposure, but also doesn't damage photomask like proximity method.

Figure 2.3.2. Different methods for lithography printing.²⁴

As our fabricated devices contained nanowires and thin plates within few micrometres width, the mask alignment process turned out to be one of the most difficult jobs. We have mentioned before that we tried to drip few nanowires onto the SiO_2 substrate. It's better to pick before photoresist coating on which nanowire the electrical device must be fabricated.

Otherwise searching appropriate nanostructure with low optical microscope illumination and magnification on photoresist coated substrate can consume lot of time, also lead to picking undesired samples due to bad visibility. We have picked and appointed location of the nanowires before spin coating using conventional optical microscope. It should be noted this procedure shouldn't be carried out after spin coating, because if your microscope is not specialized for photoresist it will expose it. Later when aligning photomask and substrate we already knew the location to be exposed, thus it saves lot of time and work. During the alignment we kept some small gap between photomask and photoresist in order to be able to move. After the desired pattern on photomask and nanowire sample were brought together the gap was closed followed by UV exposure.

Another advantage of the negative photoresist is the reverse photomask patterning compared to the positive photoresist. The dark patterns in photomask for positive resist are oppositely transparent for negative, while transparent areas are dark in negative photoresist. For the positive photoresist during microfabrication we want to expose few micrometres area and develop it, meaning this area in photomask is going to be transparent while other places dark. During the mask alignment we have to use this few micrometres transparent area to find tiny nanowire and align it. This is actually quite a big disadvantage for our project, which makes practically impossible to see nanowire through 2-3 μm openings in the photomask. While in the negative photomask few micrometer area to be developed appears dark in the photomask, and all other area is transparent. This gives us large transparent area on the photomask, which makes our task to align much easier.

Figure 2.3.3. UV lithography exposure in contact, proximity and projection methods. (Diagram courtesy of Georgia Tech)

There is also another important aspect of the photoresist exposure. The UV light in the photolithography process is monochromatic. It's projected vertically upon the photoresist inside the machine, but even though the incident light will have different angles. This light will travel through the photoresist and strike the substrate surface, in most of the cases the substrates are strongly reflective, especially for glass. The reflected light will travel back to the top of the photoresist, where it interferes with the new incident light's particles. This interference forms regions of high and low intensity within the depth of photoresist, so called standing wave formation. After the developing process the sidewalls of the obtained patterns will exhibit the standing wave patterns, that will look like a ridges. For fabrication of few micrometre structures these standing waves must be addressed properly. One of the solutions to prevent standing wave effects is to apply thin absorbing layer upon the substrate, which is called bottom antireflective coating (BARC).

2.3.5 Post bake

The post bake process is only required for negative and image reversal photoresists. While positive photoresist can proceed to developing right after the UV exposure. One important advantage of the post baking is that it can reduce effect of standing waves. The reason behind this phenomenon is still unclear, some believe that at high temperature the resin diffuses and transforms the ridges on sidewalls into smooth walls. But the main application of this step is to create solubility differential between exposed and unexposed areas in photoresist. We have already clarified earlier the exposed areas in the negative and image reversal photoresists become insoluble. The chemical compounds after first exposure generate some small acid, and then during post bake these chemical compounds start active reaction with polymer resin. Eventually the polymer resin in photoresist turns insoluble in exposed parts. These chemical reactions can be activated only within temperature range 110-130° C. If the temperature is too low, even highly exposed photoresist can't be converted. At high baking temperatures the PAC photoresist will start to thermally decompose, no matter exposed or not. Without PAC the developing of the photoresist will significantly suffer.

It's necessary to wait few minutes before starting post baking, because during the first exposure there was N₂ gas formation within the photoresist. Within few minutes in the air significant part of the N₂ will outgas from the resist. If this step is skipped, during the baking N₂ gas will start bubbling and foaming, destroying the uniformity of resist film.

In the chapter of prebake we have discussed the importance of drying photoresist. But some small concentration of water in the photoresist is important, as long as resist appears solid and hard¹⁶. This is to achieve reasonable high development rate and contrast. After baking process is performed, the photoresist can be left in the air for a few minutes. The humid air will diffuse some water into the photoresist. It takes about 10s to rehydrate 1μm

thickness photoresist, and 10 min for 7 μ m film. So the rehydration time must be adjusted according to the resist film thickness. In the end high development rate will allow us to spend less time for developing, especially if there 10-20 samples in the same batch. Also rehydration provides better pattern profile. The total dark erosion near the top of the sidewalls is reduced substantially.

2.3.6 Second exposure

The following step is required only for the image reversal photoresist. Since this photoresist behaves at the beginning like positive photoresist, it's insoluble initially. The first exposure is usually done for a small amount of time just to break chemical bonds for certain PAC. After post exposure the exposed areas are cross-linked and become totally UV inactive and insoluble in the developer. Meaning if we expose these areas again for a small amount of time then they won't be affected. For this process then we don't require photomask, and whole photoresist can be exposed for sufficient time. During second exposure the parts of resist non-exposed first time will generate carboxylic acid and become soluble for development. No alignment requirements allow us to expose all samples in one time.

2.3.7 Developing

Together with the mask alignment the developing process is also a crucial step in the photolithography fabrication. Frequently used developers are based on aqueous bases. The control parameters of this process are quite critical, but flexible as well. So before one starts development he must calibrate all developing parameters as precise as possible. The obtained pattern on photoresist is more affected by handling during developing, rather than exposure settings. The development rate is mainly depends on the type of photoresist used and post baking parameters. If the resist is baked for a too long time, or high temperature, then large

portion of the photo active compound will be decomposed. The second exposure won't be able to generate enough carboxylic acid to make it soluble.

There are different methods of applying developer solution to the photoresist samples, like "shower" spray or puddle. For the mass production of wafers in the industry they usually soak large amount of wafers into the developer. But in our project we have done mask alignment one by one for different nanowires. Depending on the location of the nanowire, how the spin coating and baking was done, majority of the sample have shown differences in the developing properties. It's convenient to dilute the developer solution with the DI water, in this way we can control the developing speed. From our observation too long developing time doesn't provide good pattern profile, while too fast developing is critical to control, when few seconds of overdeveloping can totally destroy desired pattern. Usually developing time within the range 20-30 seconds have provided good control over this process.

The underdevelopment is definitely unacceptable for most of the fabrication projects. Because organic left-over from photoresist are going to significantly affect the quality of the contact deposition in later steps. It's more preferred to overdevelop the sample rather than under develop. The degree of over developing gives us interesting prospective. We can create some specific structures other than vertical sidewalls. For the positive photoresist with overdeveloping the top of the sidewalls will further continue to develop and they'll dissolve faster than the bottom. This in the end presents a structure of overcuts. Interestingly the negative and image reversal photoresists provide undercut profile for over developing. By overdeveloping we can control the size of the overcuts and undercuts for the pattern, the benefits of these structures mainly go for lift-off process. It must be noted that it shouldn't be overdeveloped too much, otherwise whole photoresist will start to dissolve, which ends in erosions and organic contaminations in the final pattern.¹⁷

Figure 2.3.4. Strong and weak undercut during photoresist developing.

2.3.8 Contact deposition and Magnetron Sputtering system

After the desired pattern has been obtained on the photoresist using UV photolithography process, we can proceed to transfer this pattern to the substrate itself. There are mainly three methods for this purpose: etching, deposition and ion implantation. These methods serve different purposes in the device fabrication. In our projects we mainly required contact deposition on the patterned photoresist with the help of Magnetron Sputtering system.

Magnetron sputtering deposition is physical vapor deposition (PVD) method for deposition of films on substrates. It involves creating plasma with positively charged particles and accelerating them towards charged electrode target. The positively charged ions strike the surface of the negative electrode, dislodging and ejecting atoms from it. These ejected atoms further deposit around the system including the substrate. Sputtering deposition is the frequently used physical vapor deposition technique, alongside with pulsed laser deposition (PLD). For the contact deposition lot of laboratories use evaporation method as well. The advantage of sputtering method is that the plasma can eject atoms from any target, while the

temperature of the target generally can be kept at room temperature. For the evaporation methods, the thermal heat must be sufficient enough to melt the source, thus this technique more troublesome for materials with high melting temperature. Also the deposition rate and thickness for the sputtering method can be done more precisely. And the quality of the deposited film is as good as the target's quality. For metallic contacts some may not consider how good deposition goes, but for high quality thin films the sputtering system is definitely good choice. The contacts deposited using sputtering generally have better adhesion to the surface, which is crucial in fabrication of nano- and microdevices. Because the contact area for these devices is extremely limited, if contact is not deposited well enough then the signal obtained from measurement will have larger noise level. If contact is deposited too badly, it may as well removed by lift-off. For sputtering system the deposition can be done with target at bottom and substrate at top, or reverse, while in other techniques they require fixed position, like in evaporation where the source has to be at bottom. The main disadvantage of this process that the deposition of material is same in all directions, it's not possible to control where to deposit the given thin film. Since the deposited material diffuses along the surface of substrate, later it makes lift-off process more complicated.

Figure 2.3.5. Schematic view of sputtering deposition. (Diagram courtesy of Clear metals Inc)

The plasma in the sputtering system is supplied by DC, AC or RF power supplies depending on the type target material. The chamber of the sputtering system is generally kept at high vacuum and uses loadlock to transfer the samples into the main chamber. In opposite situation one has to open main chamber everytime to load and unload the samples. This will consume lot of time to pump down the chamber and also carries high risk of contamination. After sample is loaded and high vacuum is reached, we can proceed for deposition. Firstly the inert gas is given to the chamber at constant flow rate. Preferred inert gas is argon, because these atoms don't form reactions with deposited material and substrate. Also argon atom is heavy and produces high sputtering and deposition rates.

Target material is set to negative voltage (cathode), while substrate is at positive voltage (anode). This voltage difference will accelerate free electrons in the system, and then these highly energetic electrons will collide with the Argon molecules and drive their electrons as well. In the end argon atom is left positively charged. Excess positively charged molecules will be driven towards cathode and start continuous bombardment. The atoms in the target

material will be dislodged and ejected into the chamber. These target molecules will diffuse around the chamber and deposit everywhere, as well as on the substrate. There is permanent magnet located behind the target source. When the plasma is created inside the sputtering chamber, this magnet will help to confine the plasma around the target material. Some free electrons will eventually find their way back to the argon molecule and fill hole in the electronic shell. Since this electron was accelerated and gained some energy, the excess energy will be released in the form of photons. The result of continuous photon release is plasma.

It's critically important to keep the substrate surface as clean as possible. The adhesion of sputtered atoms to substrate will be strongly affected by any type of contamination on the surface. So it's important to get rid of organic contamination during development. For the oxide sample oxygen plasma is an effective tool to clean the surface area for contact. But some material's quality is sensitive to the oxidization level, which doesn't allow use of oxygen plasma. For those materials argon plasma cleaning can be applied, but argon plasma must be set to mild parameters, otherwise it can cause ion implantation, structural disorder for the sample. Thus it's very important to carry out developing procedure successfully, because later we can't apply standard acetone, IPA solutions for cleaning. The patterned sample can be either flushed with DI water, or soaked into acid solution.

2.3.9 Lift-off process

Lift-off is the final step in the photolithography fabrication. It involves removing all remaining photoresist from the substrate. There are two commonly ways of resist removing: wet stripping and dry stripping. The wet stripping involves organic or inorganic solution to dissolve remaining photoresist, and dry stripping is done by plasma. The most frequently used method in laboratories is wet stripping with acetone. But disadvantage of the acetone is

that it can leave some contamination on substrate. The sample can be further soaked into the IPA to achieve cleaner surface. Though for wafer processing in the industry other types of wet etching are used, like phenol-based strippers. Due to the photoresist hardening coming from UV exposure, or harsh processing methods, it has been difficult to remove photoresist by means of chemical solutions. Cleaning substrate surface from resist scum can be further achieved using plasma etching, though in some cases plasma can't be applied, like in graphene based devices.

In our projects we also made use of acetone as our wet stripping solution. For the lift-off samples are be put into the acetone from few minutes up to several hours. If the deposited material is too thick, of course it's better to keep in acetone longer. The optimal time may need to be found for some materials, because acetone can etch the material as well. It's important to take out samples after whole resist has been dissolved. If the sample is dried with nitrogen gas with some leftover photoresist, then this resist cannot be removed again by wet stripping. And it should be noted to check the level of acetone liquid used for lift-off. It's highly volatile solution and during long lift-off process it can evaporate entirely. In that case lift-off samples will be extremely contaminated and can't be used.

As we mentioned earlier one of the disadvantages of sputtering method is the uniform distribution of deposited material in all directions. Thus target atoms will be also deposited into sidewalls of photoresist patterns, which complicate our lift-off process significantly. For this problem the thickness of the contact deposition must be optimised. Too thin deposition we may not achieve good contact and it also difficult for wire bonding of sample. If contact is too thick, it will be too heavy and break adhesion bonds during lift-off. For our photoresist thickness 1.4 μm the range of deposition thicknesses 50-200 nm were found to be good for handling purposes. Some devices consist of very fragile nanowires that could easily break during lift-off, while some flakes can be too strong to break contact bonds instead. Either way

for these samples milder lift-off process should be applied. After whole photoresist has been dissolved we generally shake samples inside the acetone to remove remaining deposition flakes. Then using acetone bottle we can as well flush sample with little acetone pressure. In most of the cases it's enough to lift-off. If lift-off is not achieved ultrasonication can be applied that can perform this task successfully, but as mentioned earlier the device can be broken easily.

We have discussed about overcuts and undercuts generated using different type of photoresists. The undercut structure suggests favourable advantage for the lift-off process. During the contact deposition in sputtering system atoms will deposit in all sides. But in undercut structure the materials deposited at the top and bottom of the sidewall are less likely to attach to each other. While in overcut structure they will definitely attach and complicate the lift-off process.

2.3.10 Photolithography parameters used in our projects

Fabrication of the Ag₂Te devices is performed using standard photolithography method with the SUSS MicroTec MJB4 Mask Aligner system. The system is one of the convenient tools in terms of the high precision, performance and reliability. This equipment is able to achieve the resolution as low as 1µm, under the vacuum contact even as low as 0.5µm. Manual mask aligner is more convenient in our research compared to other lithography setups like EBL, E-Beam writer, etc. because it's consumes less time for fabricating the device. Another advantage is we can easily calibrate all the parameters of the photolithography. The choice of our photoresist was AZ5214E, which is Image Reversal Photoresist. This particular photoresist could be utilized as positive or negative photoresist. For the fabrication of nanodevices, where the sample size can be only few hundred

nanometres, it's much convenient to use negative photomask, which has larger transparent area for the alignment. Thus we have been using our AZ5214E as negative photoresist.

Fig.2.3.1 demonstrates all the crucial steps of the photolithography patterning. The details are as follows

1. 300nm p-type SiO₂ substrates were cut into $\sim 2 \times 2 \text{ cm}^2$ pieces, and then cleaned with acetone (15 min) and IPA (15 min). For Ag₂Te nanowire devices 1-2 μl nanowire-IPA solution was dripped upon SiO₂ substrates. For BiSbTeSe₂ devices the sample flakes were transferred using mechanical exfoliation.
2. AZ5214E photoresist has been spin coated on samples for 4000 rpm, 30 sec. The resulting resist film is about 1.4 μm thickness.
3. Prebake has been done at hotplate set to temperature 105° C for 105 seconds.
4. The first UV exposure for 1.8 seconds.
5. Post exposure bake inside the oven set to temperature 110° C for 7 min 30 sec.
6. Second exposure for 25 seconds.
7. AZ developer and DI water were mixed at equal ratio. Total developing time is about 18 seconds.
8. Contact deposition was carried out inside magnetron sputtering system with a base pressure of 1×10^{-8} tor. Metallic contacts deposited were Cr/Au (5 nm/100 nm).
9. Lift-off with acetone at least for half an hour.

2.4 Electrical Measurements

Our project mainly focuses on the low-temperature electrical measurements on the TI devices. The physical quantum phenomena related to the topological insulator system are

clearly detectable at low temperature regime. Thus we have been performing our experiments on the Physical Property Measurement System (PPMS). Our PPMS is a cryogenic system with a 9 T superconducting magnet. Using different options, the PPMS can be used to measure magnetic, electro-transport and thermo-electric quantities. The variables in the PPMS system can be controlled by the user, as well as automated to some degree. The measurements can be carried out using specially designed measurement options within the PPMS, or desired instruments can be integrated into the system. The controlled magnetic field for our system can go to 9 T, and temperature range for the PPMS is 2 to 400K. This allows us to mount devices at room temperature, and then cool down to low temperature regime. The temperature sweep control in the PPMS system can go as low as 0.01 K/min, which makes this system one of the best candidates for temperature variable measurements. Another advantage of PPMS is its PC controllable option, so the measurement steps are programmable into long sequences using MultiVu software. The data obtained from experiments can be viewed in a graphic, tabular, or raw data format in the MultiVu. If the third party instruments are installed, they also can be integrated with MultiVu software. The PPMS system can carry out measurements 24 hours a day, 7 days a week. For the time consuming measurements this option of the PPMS becomes invaluable in the research. All these user friendly options in the PPMS give comfortable ground for the research.¹⁸

Fig. 2.4.1 shows the schematic diagram of the PPMS probe. At the bottom of the sample chamber is a 12-pin connector pre-wired to the system electronics. This connector allows you to plug in a removable sample insert or sample “puck” and offers convenient access to electrical leads for application hardware and electronics. This connector provides the foundation for all of the PPMS measurement inserts. The suppliers can provide sample pucks designed specifically for the PPMS, but the connector design is also friendly for user-designed inserts.

Figure 2.4.1 The schematic diagram of the PPMS probe and cross section view of the PPMS chamber.(Diagram courtesy of Quantum Design Inc)

The chamber of the PPMS is sealed and can be attained up to 0.1 mTorr vacuum via cryopump. The system is cooled by liquid nitrogen and helium, a vacuum pump circulates the gas from helium into the annular region, where the temperature around the device is set by system heaters. The thermometer is located at the bottom of the chamber as shown in Fig. 2.4.1 For the probes inserted into the chamber the device might be a bit far from the system thermometers, so temperature gradient will give differences in actual and recorded temperature. In these situations user controlled thermometer was integrated into the probes, where thermometer was located in the vicinity of the sample under measurement.

The quantum design AC measurement system (ACMS) option for the physical property measurement system is a versatile DC magnetometer and AC susceptometer. The ACMS contains a detection coil set that inductively responds to combined sample moment and excitation field. The noise from uniform background sources is eliminated by arranging the detection coil in a first order gradiometer configuration. The detection coil set is surrounded by the AC-drive coil that provides an alternating excitation field of up to 10 Oe in a

frequency range from 10 Hz to 10 kHz. The copper drive and detection coils are situated with the ACMS insert, concentric with the superconducting DC magnet of PPMS.

The DC moment is measured by the extraction method. During DC measurement a constant field is applied to the measurement region and the sample is moved quickly through both sets of coils, inducing a signal in them according to Faraday's law,

$$\varepsilon = -\frac{d\Phi}{dt} \quad (2.4.1)$$

where ε is the electromotive force and Φ is the magnetic flux.¹⁸

2.4.1 Electrical measurement setup

The classic laboratory electrical measurements are carried out using four-point-probe measurement technique, or similar task can be done by two-point-probe method. These methods serve resistivity measurement purposes mainly. Some modifications can be done to perform other type experiments. Though the geometry of the two-point-probe method is simple, the final measurement is affected by the lead and contact resistance, as given in the measured resistance

$$R_{measured} = R_{lead1} + R_{contact1} + R_{sample} + R_{lead2} + R_{contact2} \quad (2.4.2)$$

In the measurement of low resistance samples the contribution of the lead and contact resistances can be significant, which is considered the main drawback of the two-point method. For some sample soldering voltage and current contacts into the same place can be difficult, resulting in bad contact. The overheating due to bad contacts can lead to injection of impurities or burning fragile sample. The collinear four-point-probe method is more preferred to carry out low-noise measurements. This technique involves separate current carrying and voltage sensing electrode, and eliminates impedance of the wire and

contact resistance. Ideally all four probe contacts must be spaced at equal distances from each other. When the current is driven through the sample, the potential drop across two arbitrary points is acquired using voltmeter. The inner voltage contacts draw no current due to impedance. The resistance of the sample can be calculated using standard Ohm's Law

$$\rho = \frac{RA}{l} \quad (2.4.3)$$

where ρ , R , A , l are the resistivity, resistance, cross-section and distance between voltage contacts. This measurement technique can provide accurate results for the 1D structure, like nanowire. But generally samples are from variety of structures and shapes, where designing four-probe contact can be tricky sometimes because they must be placed in a straight line. This geometry is difficult to implement into the samples with arbitrary shape, anisotropy. Also both given methods require a condition of uniform resistivity distribution.

In the Hall Effect measurements the geometry of the contacts are altered as in Fig. 2.4.2. In this setup the voltage contacts are located in the transverse way to the current direction. It's quite important that the Hall measurement geometry is set properly; slightest misplace of the contacts can lead into resistivity contribution to the Hall voltage. The Hall measurements also have similar drawbacks related to the samples shape and uniformity, as discussed for previous methods.

Figure 2.4.2 Schematic view of the Hall measurement setup.

2.4.2 Aharonov-Bohm oscillations

In our first project, Ag_2Te nanowires were used to probe Aharonov-Bohm quantum interference. For these experiments, we require low temperature regime and low magnetic field sweep. Because the phase memory of the electron wave particles is limited by the magnetic field, at high fields we quantum interference is destroyed. Most of the measurements were carried out at 0 - 2 T range. To probe AB oscillations we need magnetic field parallel to the driven current along the length of the nanowire. The schematic diagram of the AB measurement setup is shown in Fig. 4 (Chapter 3)

The magnetic field inside the PPMS chamber is in vertical direction inside the chamber. And we require the nanowire sample mounted along the magnetic field. For this purpose we have used horizontal rotator, which is a PPMS probe. The horizontal rotator probe is designed to allow sample puck to rotate around the axis perpendicular to the magnetic field. Nanowire is mounted on the puck and inserted into the horizontal rotator. Further horizontal rotator is inserted into the PPMS chamber and sealed. After that the puck can be rotated to set the magnetic field and nanowire length in the same direction. The alignment for this measurement is very critical.

Horizontal rotator probe has different designs of sample pucks suited for it. The sample puck used in our experiments is shown in Fig.2.4.6 Inside the chamber this puck will rotate along y -axis. The device with the sample is mounted as shown in Fig. 2.4.5, so the surface normal of the device substrate will be along x -axis. It's important to mount the device into the puck, such that it will be as flat as possible. For this purpose we have applied double sided tape onto the flat surface of puck. Further device was attached into the tape. When the probe is inserted into the chamber the device is rotated around y -axis at certain magnetic field to achieve the minimal resistance value of the sample. Because when the nanowire length and magnetic field are in the same direction, the magnetoresistance must show its minimal value.

The measurements were taken using standard four-point-probe resistivity measurement technique. The current used in experiments was 300 nA AC current. This current was chosen an optimal value for nanowires, because it was large enough to obtain reasonable noise level. At higher current values it's possible to achieve lower noise level, but there is risk of sample burning due to the fragile nature of nanostructures. For too low current values the noise level is larger than the signal of AB quantum oscillations. Generally AB quantum oscillations in our experiments were $\sim 0 - 1.5\%$, which really requires us to achieve high quality samples and good fabrication, measurement procedures.

Figure 2.4.4 Horizontal rotator probe. (Diagram courtesy of Quantum Design)

Figure 2.4.5 Side view of the horizontal rotator probe. (Diagram courtesy of Quantum Design)

2.4.3 Ag₂Te thin film measurements

Using our CVD growth methods we have obtained variety of Ag₂Te structure shapes. The largest nanoribbons or nanoplates obtained in our experiments were as large as 10-20 μm width. In our further experiments we have analysed the Hall, magnetoresistance, angle, gate voltage, and temperature properties of different Ag₂Te samples grown by CVD method. Since some of the experiments we wanted to do with varying angle, for the convenience all measurements were carried out using horizontal rotator probe in the PPMS. Because with the help of horizontal rotator we were able to carry out all measurements we needed. The gate voltage source for our experiment was integrated into the PPMS, since the PPMS system doesn't originally have gate voltage option.

The sample puck (Fig. 2.4.6 (a)) for the horizontal rotator in these experiments is different than for AB oscillations probing experiment. This puck allows the magnetic field to be projected on top surface of the nanoplates. And it still can rotate around the y -axis. The gate voltage system for our experiments is shown in Fig. 2.4.6 (b). The measurements were carried out at current 300 nA, while the gate voltage range was chosen 0-50 V. These fragile nanostructures are sensitive to the gate voltage, majority of the samples are bound to burn at +100 V gate voltages. Thus we decreased our measurement range into the safe values. Also the abrupt changes in voltage values can also lead to burning of the sample.

Figure 2.4.6 a) Sample is wired to the PPMS sample holder. b) Schematic representation of the sample device.

2.4.4 Anisotropic magnetoresistance (AMR) measurements

The AMR effect is due to the spin-orbit interaction in the material. Electrical resistance originates from the electron scattering by phonons, magnons, impurities and other electrons. The scattering probability is different along different directions because wavefunctions of the electrons are not symmetric, and therefore the resistivity along different directions is different. So for the AMR measurements we are going to carry out angular dependence of the resistivity at different magnetic fields. The diagram for an AMR measurement is given in Fig. 2.4.7. In an AMR measurement standard four-point-probe resistivity measurement technique

was applied in an external magnetic field. For this experiment we are going to use the same setup as for AB quantum interference nanowires with external gate voltage. The resistivity changes with the relative orientation (θ) of the current and magnetization

$$\rho(\theta_{M,I}) = \rho_0 + \rho_{\Delta} \cos^2(\theta_{M,I}) \quad (2.4.6)$$

where ρ_0 is the zero-field resistivity and

$$\rho_{\Delta} \equiv \rho_{\parallel} - \rho_{\perp} \quad (2.4.7)$$

where parallel and perpendicular components refer to the relative orientation of the in plane magnetization and the current flowing in the material.²⁰

Figure 2.4.7 Diagram of the Anisotropic Magnetoresistance measurement.

Reference

1. H. J. Choi, *Springer-Verlag Berlin Heidelberg* (2012)
2. S. Wagner, W.C. Ellis, *Appl. Phys. Lett.* **4**, 89 (1964)
3. Laboratory safety manual, *Princeton University*
4. RCA clean, *Colorado school of Mines*. Available from:
http://www.mines.edu/fs_home/cwolden/chen435/clean.htm
5. J. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, C. Fiori, E. Lifshin, *New York: Plenum Press*. (1981)
6. T. E. Everhart and R. F. M Thornley, *Journal of Scientific Instruments* **37**, 246–248 (1960)
7. J. Goldstein *et al*, *Springer* (2003)
8. W. R. Herguth *et al*, *SGS Herguth Laboratories, Inc.* (2012)
9. B. Cappella, G. Dietler, *Surface Science Reports* **34**, 1–104 (1999).
10. Q. Zhong, D. Inniss, K. Kjoller, V. Elings, *Surface Science Letters* **290**, 688 (1993)
11. E. Ruska, *Microsc Acta Suppl.* (1980)
12. D. B. Williams, C. B. Carter, *Springer* (2009)
13. Spin coating of photoresist, *MicroChemicals Inc* (2013). Available from:
http://www.microchemicals.com/technical_information/spin_coating_photoresist.pdf
14. Baking & Delays, *MicroChemicals Inc* (2003). Available from:
http://www.microchemicals.de/secret/baking_and_delays.pdf
15. Resists, Developers and Removals, *MicroChemicals Inc.* (2013). Available from:
http://www.microchemicals.com/technical_information/resists_developers_removers.pdf
16. Rehydration of Photoresist, *MicroChemicals Inc* (2013). Available from:
http://www.microchemicals.com/technical_information/photoresist_rehydration.pdf
17. Lift-off process with Photoresist, *MicroChemicals Inc* (2013). Available from:
http://www.microchemicals.com/technical_information/lift_off_photoresist.pdf
18. Quantum Design PPMS manual, *Quantum Design Inc.* (2008)
19. Low level measurement handbook, *Keithley Inc* (2003)
20. T. R. McGuire and R. I. Potter, *IEEE Transactions on Magnetics* **11**, 1018 (1978)
21. J. Palisaitis, R. Vasiliauskus, *Phys. of Advanced Mat. Winter school* (2008)
22. D. A. Muller, *Nature Materials* **8**, 263 - 270 (2009)
23. Available from: <http://cimewww.epfl.ch/people/cayron/Fichiers/thesebook-chap3.pdf>
24. Available from: <http://www.lithoguru.com/scientist/lithobasics.html>

Chapter 3. Aharonov-Bohm quantum interference in β -Ag₂Te nanowires

The β -Ag₂Te material has been proposed theoretically to be a new topological insulator system, but so far there were no experimental evidences to support that prediction. In this chapter we are going to present experimental evidences of existence of surface states in Ag₂Te nanowire samples. The content of this chapter involves the motivation (section 1), band structure calculation (section 2), material fabrication and characterization (section 3), and Aharonov – Bohm quantum interference measurements (section 4), ambipolar gate effect (section 5), temperature dependence results for our devices.

3.1 Introduction

Today topological insulator is a trend research field in the condensed matter physics. It promises great potential application in various fields, like spintronics and quantum computation. Our first steps in the topological insulator research were to find a topological insulator material for our research. So far various two- and three-dimensional topological insulator systems have been proposed via band structure calculation. However, up to date, only CdTe/HgTe/CdTe^{4,5} and InAs/GaSb⁶ quantum well structures have been experimentally confirmed to be two-dimensional topological insulator while strained HgTe^{7,8} and several Bi based compounds, such as Bi_xSb_{1-x}, Bi₂Se₃, Bi₂Te₃,⁹⁻²⁰ have been confirmed to be three-dimensional topological insulators. Thus, researchers are still exploiting and identifying other good candidates of topological insulators with special characteristics. We decided to concentrate on the newly proposed β -Ag₂Te material as topological insulator.

β -Ag₂Te, a narrow band gap nonmagnetic semiconductor, shows unusual large and nonsaturating quasi-linear magnetoresistance in the field range of 10-10⁵ Oe and the temperature range of 5-300 K^{21, 22}. The origin of the unusual magnetoresistance has generated debates since its discovery²³⁻²⁵. β -Ag₂Te was predicted to be a topological insulator with gapless Dirac-type surface states via band structure calculation²⁶. It was proposed that the observed unusual magnetoresistance may largely come from the surface or interface contribution. The characteristic feature of this new binary topological insulator is a highly anisotropic Dirac cone. So far, the topological surface states of β -Ag₂Te and Bi₂Se₃ (221) surface⁴³ have been predicted to be highly anisotropic. Physical realization of topological insulator with highly anisotropic Dirac fermions may lead to a discovery of novel electronic states and long spin relaxation time in topological insulators²⁷. The long spin relaxation time is extremely important for the application of topological insulator in spintronics, which has barely been studied so far.

In order to verify the essential features of the aforementioned picture, we utilized a different method to perform band structure calculations and carried out magnetotransport and gated electric transport experiments on single crystalline β -Ag₂Te nanoribbons. Our calculations confirmed the anisotropic topological surface state, although the shape of the surface state of our calculations is different from that in the literature²⁶. The existence of the surface states in Ag₂Te is confirmed experimentally, based on the Aharonov-Bohm interference pattern obtained in the magnetotransport measurements at low temperatures. It is further supported by the ambipolar electric field effect for devices fabricated by β -Ag₂Te nanoribbons.

3.2 Band structure calculation

Band structure calculations have been carried out by the group of physicists led professors Shen Lei, Feng Yuan Ping and their student Wu Qingyu from Department of Physics, National University of Singapore. Our density functional calculations were carried out using the Vienna ab initio simulation package (VASP)²⁸ with projector augmented-wave potentials²⁹ and the Perdew-Burke-Ernzerhof generalized gradient approximation³⁰ for exchange-correlation functional. The Hamiltonian contained the scalar relativistic corrections and the spin-orbit coupling was taken into account by the second variation method³¹. The lattice constants of β -Ag₂Te were adopted from experiments³². The generic β -Ag₂Te substrate was modeled by a slab of 48 atomic layers or 12 unit cell layers along the hexagonal c -axis²⁶. The slab calculations presented in this work were performed using symmetric setups, so the upper and lower surfaces were identical and their energy bands were degenerated. The vacuum layers were over 20 Å thick to ensure decoupling between neighboring slabs. The cutoff for plane-wave expansion was set to be 300 eV and a 7 x 7 x 1 k-point mesh was used for the surface unit cell. In the band structure calculations of Zhang *et al*²⁶, first-principles calculations were utilized in the bulk state of β -Ag₂Te, while tight-binding method was employed to calculate the surface state. To keep the calculations consistently and improve the accuracy of description of the surface state, we used first principles calculations for both bulk and surface band-structure calculations.

Fig. 3.2.1 shows the calculated surface band structure of β -Ag₂Te with spin-orbital coupling (SOC) included and the out-of-plane of the surface is along the c -axis. The shaded area is the bulk band structure projected to the 2D Brillouin zone. It is seen that the bulk gap is around 0.1 eV which is in good agreement with experimental data^{33, 34}. The upper inset shows the shape of the 2D Brillouin zone for the surface unit cell. The red solid lines are the surface topological state, which show a single Dirac cone on the surface, which is similar to

that obtained via tight binding method²⁶ although the shapes of the surface state are different. The bottom inset shows the constant-energy contours which cut through the surface state below the Dirac point at energies of -10 meV, -20 meV and -30 meV. The red (blue) color means the out-of-plane components pointing out-(in-) ward of the plane. The color scale, with blue and red, indicates the intensity of negative and positive values representing the projection S_z . Our results show that the spin direction of the surface states precesses counterclockwise around the Γ point below the Dirac point and has out-of-plane component. The most interesting phenomenon is the anisotropic surface Dirac cone of β -Ag₂Te which is different from the round and warped hexagonal surface state of Bi₂Se₃ and Bi₂Te₃^{10, 35}. It is because of the absence of the rotational symmetry in β -Ag₂Te.

Figure 3.2.1. The calculated surface band structure of the β -Ag₂Te film with the projected bulk band structure in the background (blue) to the 2D Brillouin zone whose shape is shown in the upper inset. The surface topological states are highlighted by the red lines. The bottom inset shows the expectation values of spin operator (S_z) of the surface band in β -Ag₂Te along k_x and k_y directions in momentum space. Three constant-energies, which cut through the surface state below the Dirac point, are plotted. The red (blue) color means the out-of-plane components pointing out-(in-) ward of the plane. The color scale, with blue and red, indicates the intensity of negative and positive values representing the projection S_z .

3.3 Device fabrication and characterization

Ag₂Te nanoribbons were synthesized by CVD method described in Chapter 2 inside a 30 cm horizontal tube furnace equipped with a 3 cm diameter quartz tube. The powder of Ag₂Te (Sigma-Aldrich, 99.99%) was used as a precursor placed at the hot center region. As

grown ribbons are typically 100-200 nm thick, 100 nm to several micrometers wide, and up to tens of micrometers long.

TEM characterization was done in Institute of Materials Research and Engineering by Professor Han Ming Yong and his student Zhang Shuang Yuan. The Ag₂Te sample for TEM has been prepared using Focused Ion Beam by Professor Yu Ting. For the sample quality characterization we have performed transmission electron microscopy (TEM). TEM images were examined by Philips CM300 field emission gun transmission electron microscope operating at an accelerated voltage of 300 kV. The deposited nanoribbons on the sapphire substrate were placed in a vial containing 2 mL methanol solvent, and subsequently ultrasonicated for 10 min to separate the nanoribbons from substrate and disperse them into solvent. A drop of such dispersion (2 μL) was withdrawn and added onto a carbon-coated copper grid, which was placed on a piece of tissue paper. The solvent on the copper grid was immediately adsorbed by the tissue paper

Figure 3.3.1. (a) TEM image of an as prepared nanoribbon with the inset showing the corresponding SAED pattern. (b) Transmission electron diffraction pattern simulated based on monoclinic Ag_2Te single crystal with cell parameters $a = 8.164 \text{ \AA}$, $b = 4.468 \text{ \AA}$, $c = 8.977 \text{ \AA}$, space group $\text{P2}_1/\text{c}$ (ICSD file number: 073402). The electrons are directed to the sample at zone axis $[4 \bar{8} 5]$ with energy at 300 KeV. (c) High resolution TEM image of a focused ion beam milled Ag_2Te nanoribbon with the inset showing the corresponding fast Fourier transform pattern. (d) EDS mapping for Ag_2Te nanoribbon.

and ready for the TEM characterization. The atomic ratio between Ag and Te was determined by energy-dispersive X-ray spectroscopy in a scanning electron microscopy. The width and thickness of the nanoribbons were determined by scanning electron microscopy and atomic

force microscopy, respectively. The transmission electron microscopy (TEM) and corresponding selected area electron diffraction (SAED) investigation was carried out for the as-prepared nanoribbons. Fig. 3.3.1 shows a TEM image of nanoribbons. The diffraction pattern (Fig. 3.3.1(a) inset) shows clearly that the nanoribbon is single crystalline and matches well with the standard monoclinic β -Ag₂Te (ICSD file number: 073402) single crystal electron diffraction pattern (Fig. 3.3.1(b)) at zone axis $[4 \bar{8} 5]$. The electron diffraction pattern are simulated based on monoclinic Ag₂Te single crystal with cell parameters $a = 8.164 \text{ \AA}$, $b = 4.468 \text{ \AA}$, $c = 8.977 \text{ \AA}$, space group $P2_1/c$. A high resolution TEM picture of focused ion beam milled β -Ag₂Te is shown in Fig. 3.3.1(c). It is clear from the picture and corresponding fast Fourier transform pattern that our single crystalline Ag₂Te is very high quality and the growth direction is perpendicular to the $(1\bar{2}1)$ plane direction. Energy-dispersive X-ray spectroscopy (EDS) shows that the atomic ratio of Ag and Te is 2.02 (with an error bar of $\sim 0.5\%$) as shown in Fig. 3.3.2. The distribution of Ag and Te is homogeneous in the sample, as shown by the EDS mapping in Fig. 3.3.1(d). The transmission electron microscopy (TEM), corresponding selected area electron diffraction (SAED) and Energy-dispersive X-ray spectroscopy (EDS) demonstrate that high quality monoclinic β -Ag₂Te nanoribbons have been synthesized. Photolithography was used to pattern electrodes on the nanoribbons. Cr/Au (5 nm/120 nm) contacts were deposited in a magnetron sputtering system with a base pressure of 1×10^{-8} torr. Standard DC (for large nanoribbons) and lock-in technique (for thin nanoribbons) were employed to perform four-terminal magnetoresistance measurements in a 9 Tesla Quantum Design PPMS system.

The magnetoresistance and back-gating electric effect measurement results of $\beta\text{-Ag}_2\text{Te}$ are presented in this chapter. As the cross section areas of samples are important for the explanation of experiment results, the width and thickness of nanoribbons are measured using scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. As shown in Fig. 3(b), the nanoribbons exhibit uniform surfaces. Samples used for the AFM scanning vary in the thickness up to 200 nm. No samples were found to have larger thicknesses. Some nanoribbons have steps as shown in Fig. 3.3.2(b). Fig. 4(a) shows the schematic diagram of the standard four point measurements used in our experiments. Fig. 3.3.3(b) shows a scanning electron microscopic image of a typical device. A device composed of a nanoribbon and six equal-distance separated gold contacts is shown in the image.

Figure 3.3.3. (a) Schematic diagram of four contact devices used in our transport experiments. (b) A scanning electron microscopy image of device in our experiments. The image shows one nanoribbon and six gold contacts on the nanoribbon.

3.4 Aharonov – Bohm (A-B) oscillations

To probe the quantum interference effect in the β -Ag₂Te nanoribbons, we measured the magnetoresistance of a sample (cross section area: 0.191 width (W) $\times$ 0.098 thickness (T) μm^2) with the applied magnetic field parallel to the current flowing direction as shown in the schematic diagram (the inset of Fig. 3.4.1(b)). As shown in Fig. 3.4.1(a) and 3.4.1(b), pronounced and reproducible resistance oscillations with a period of 0.227 Tesla are observed at 2 K, 4 K, 6 K, 8 K and 10 K. It should be emphasized that the curves shown in Fig 3.4.1 (a) are “raw” data of resistance vs. magnetic field. The curves are shifted vertically for clarity and therefore have no unit for y-axis. No background subtraction is performed. The 2 K magnetoresistance in Fig. 3.4.1 (a) is plotted again in Fig. 3.4.1 (b) in the unit of $\text{m}\Omega\cdot\text{cm}$ for y-axis in a wider range of field from 0 Tesla to 9 Tesla. Prior to the work herein, the A-B oscillation was observed in Bi₂Se₃ and Bi₂Te₃, as shown in Fig. 3.4.2 and 3.4.3, which was regarded as one of the straightforward evidences for topological insulators³⁷⁻³⁹. In both those works the measured samples were smaller than our β -Ag₂Te nanoribbon (Bi₂Se₃ with 120 nm (width) and 55 nm (thickness), Bi₂Te₃ with 185 nm (width) and 30 nm (thickness)). The oscillation amplitude at 2 K is about 1.5% of the total resistance, which is slightly larger than observed amplitudes in Bi₂Se₃ and Bi₂Te₃ that are in the range of 1% and less. As indicated by the arrows in Fig. 3.4.1(a) and 3.4.1(b) and the FFT intensity as shown in Fig. 3.4.1 (c), there are also oscillations with a period of 0.113 Tesla overlapped on the oscillations with the period of 0.227 Tesla. At 2 K, the measurements were performed with a magnetic field ramping from 0 to 9 Tesla and then ramping back from 9 to 0 Tesla. At other temperatures, the measurements were carried out up to 2.5 Tesla. It is found with no surprise that the sweeping direction has no effect on the resistance oscillations. This kind of periodic

magnetoresistance oscillation can only be induced by quantum interference Aharonov-Bohm (A-B) effect or Altshuler-Aronov-Spivak (AAS) effect. As the cross section of the nanoribbon under measurement is $S = \text{thickness (98 nm)} \times \text{width (191 nm)}$, the corresponding A-B and AAS oscillation periods should be 0.221 Tesla and 0.110 Tesla, respectively. Considering the experimental error bar, we can therefore conclude that the oscillations in our measurements are attributed to a combination of A-B effect and AAS effect. The observation of A-B oscillations with a period of h/e unambiguously suggests the existence of conducting surface states in Ag_2Te nanoribbons, and the existence of conducting surface states on all the crystalline orientations (top, bottom and sides) provides explicit evidences for the topological origin of the surface states as expected by a topological insulator. The topological trivial surface states usually show an AAS oscillation strongly depending on the surface orientation due to bonding orientation. The existence of the A-B effect (period of h/e) at low temperature is a fingerprint of topological surface states with weak disorder, which is related to the Dirac type Hamiltonian of the helical surface state.

Figure 3.4.1. (a) Magnetoresistance of a β - Ag_2Te nanoribbon (cross section area: $0.191 \text{ width (W)} \times 0.098 \text{ thickness (T)} \mu\text{m}^2$) with an applied magnetic field parallel to the current flowing direction at temperature 2 K, 4 K, 6 K, 8 K, and 10 K, respectively. The curves are vertically displaced for clarity. A clear resistance oscillation with a period of 0.227 Tesla (h/e) is observed, as shown by the dotted lines. The arrows indicate an oscillation with a period of 0.113 Tesla ($h/2e$). (b) The plot of the 2 K magnetoresistance in (a) in a wider field range from 0 Tesla to 9 Tesla. The arrow indicates the minimums of the oscillations with a period of $h/2e$. Inset shows the schematic diagram of the measurements. (c) The temperature dependence of the FFT spectra of the quantum oscillations. Locations of h/e and $h/2e$ flux quantization are labeled. (d) The temperature dependence of the FFT amplitude of the h/e flux quantization (the A-B effect). The solid line is the curve of the $T^{-0.5}$ power law. (e) The ratio of the amplitude of two FFT peaks ($A(h/e)/A(h/2e)$) at different temperatures. The power law fitting gives $\sim T^{-0.38}$.

Figure 3.4.2. **a**, Schematic diagram of 2D topological surface states of a layered Bi_2Se_3 nanoribbon under a magnetic field along the ribbon length. The red and black arrows correspond to the electric current and magnetic field lines, respectively. The two cones on the top and side surfaces illustrate the Dirac surface states propagating on all surfaces with linear dispersion. The green loops encircling the same magnetic flux stand for phase-coherent paths through which the surface electrons interfere. **b**, SEM image of a Bi_2Se_3 nanoribbon, 120 nm in width, contacted by four Ti/Au electrodes. The thickness of the nanoribbon is measured by AFM (a line cut in the inset) to be 55 nm. The measurement error bars from both SEM and AFM are within 5–10%. **c**, Normalized magnetoresistance of the nanoribbon in radial magnetic fields at 2 K. A clear modulation of the resistance with a period of 0.62 T is observed, corresponding to one flux quantum (h/e) threaded into the cross-section of the nanoribbon. The solid red trace (up sweep) was taken with a scan rate of 3 mT s^{-1} and the dashed black line (down sweep) at 10 mT s^{-1} . **d**, Magnetoresistance in the full field range of $\pm 9 \text{ T}$. Inset on the left, magnetic field position of well-developed resistance minima. Inset on the right, FFT of the derivative dR/dB in the entire field range. Locations of h/e and $h/2e$ flux quantization are labelled. (Peng *et al*)³⁷

Figure 3.4.3 a, Magnetoresistance plots (resistance R versus applied magnetic field B) with superimposed Aharonov–Bohm oscillations in Bi_2Te_3 at five different temperatures between 1.4 and 8 K, and no gate voltage. **b**, AB oscillations can be clearly seen when the smooth magnetoresistance background is subtracted from the plots in **a**. **c**, Magnetoresistance plots at seven different gate voltages between -60 and 60 V, at 1.4 K. **d**, Significant enhancement of the AB oscillation for positive gate voltages can be clearly seen when the smooth magnetoresistance background is subtracted from the plots in **c**. **e**, FFT of the magnetoresistance plots in **a** reveals AB oscillations with periods of h/e and $h/2e$, suggesting different interference paths during in-plane transport. The peaks at h/e and $h/2e$ are most pronounced at 1.4 K. **f**, Amplitude of the FFT spectra in **e** versus temperature: the amplitude, fitted to $T^{-1/2}$ (red line), suggests the absence of inelastic phonon scattering. **g**, AB oscillations with periods of h/e and $h/2e$ can also be seen in the FFT of the magnetoresistance plots in **c**. The peaks at h/e and $h/2e$ are most pronounced at a gate voltage of $+60$ V. (Xiu et al)³⁸

Recent theoretical simulations^{40, 41} proposed that the disorder and the Fermi level position can determine the oscillation period and whether the resistance has a minimum or maximum at zero flux. The conditions of showing A-B oscillation (h/e) or AAS oscillation ($h/2e$) in topological insulator nanoribbons are summarized below,

1. If a topological insulator ribbon is perfect (without disorder and doping), the transport is ballistic and the magnetotransport oscillations show a period of h/e (the A-B effect).
2. If the Fermi level passes through the Dirac point of a topological insulator nanoribbon, the oscillations always show a period of h/e (the A-B effect) at any disorder strength.
3. The Fermi level is away from the Dirac point of a topological insulator nanowire. When the electron transport evolves gradually from ballistic to diffusive with increasing disorder, the quantum oscillations in a topological insulator nanoribbon show a gradual transition from a period of h/e (the A-B effect) at weak disorder to a period of $h/2e$ (the AAS effect) at strong enough disorder simultaneously.

For a nanoribbon with trivial surface states, the period of oscillation is $h/2e$ (the AAS effect), which is a well-known knowledge in quantum transport⁴⁵. Therefore, if the oscillation period is $h/2e$ (the AAS effect), we can conclude that the nanoribbon has a trivial surface state or a doped topological surface state with strong disorder. If the oscillation is h/e (the A-B effect), we can conclude that the nanoribbon has a topological surface state. The topological surface state showing the A-B effect can be one of the three conditions, 1. without disorder for any doping, 2. without doping (the Fermi level passing through the Dirac point) for any disorder strength, 3. with weak disorder. Hence, the h/e oscillation in our experiment confirms the existence of topological surface state. Based on the theoretical analysis and our experimental results, we speculate that our Ag_2Te nanoribbon has a mediate disorder, and therefore exhibit oscillations with both h/e and $h/2e$ periods. The other possibility is that the surface state includes a dominating topological nontrivial part and a

weak topological trivial part coming from band bending at the surface, which shows A-B oscillations with a period of h/e and AAS oscillation with a period of $h/2e$, respectively.

Recently, quantum oscillations with a period of h/e were observed in InN nanowires, which have a topological trivial surface state due to band bending⁴². However, the oscillations are caused by energy level splitting and therefore their magnitude does not decay with increasing magnetic field. The magnitude of oscillations for Ag_2Te decays with increasing magnetic field, which is a standard characteristic of quantum interference induced oscillation. Therefore, the A-B oscillation (h/e period) in our measurements should be a fingerprint of topological surface state and not be the type of oscillations in InN nanowire. The decaying speed of A-B or AAS oscillation with increasing magnetic field is related to the thickness of the surface states. The decay of the oscillation magnitude with increasing magnetic field in Ag_2Te is faster than that in Bi_2Se_3 , which may indicate thicker surface states in Ag_2Te_3 . To study the evolution of the A-B and AAS oscillation with increasing temperature, fast Fourier transform (FFT) was employed to analyze the derivative dR/dB . The FFT intensity of 2 K, 4 K, 6 K, 8 K, and 10 K are plotted in Fig. 3.4.1(c), which clearly shows the coexistence of the A-B oscillation (h/e) and the AAS oscillation ($h/2e$). As shown in Fig. 3.4.1(e), the ratio of the FFT intensity of the A-B oscillation and AAS oscillation decreases with increasing temperature, which is larger than 1 at 2 K and 4 K and smaller than 1 at 6 K, 8 K, and 10 K. Our results are similar to the observed FFT intensity evolution of the A-B and AAS oscillations observed in Bi_2Te_3 shown in Fig.3.4.3 This phenomenon may be explained by the increasing electron and phonon scattering with increasing temperature. As aforementioned, when the electron transport evolves gradually from ballistic to diffusive with increasing disorder or scattering, the quantum oscillation in topological insulator will show a gradual transition from h/e period (the A-B effect) to $h/2e$ period (the AAS effect) simultaneously. Therefore, the ratio of the FFT intensity of the h/e and $h/2e$ oscillation should

decrease with increasing temperature due to the increasing scattering. The power law fitting of the temperature dependent ratio gives $\sim T^{-0.38}$.

Due to the topological surface transport, β -Ag₂Te nanoribbons actually form a two dimensional transport system. In a two dimensional electron system with high density electrons and weak electron-electron interaction, the phase coherence time $\tau_\phi \sim \hbar/k_B T$ can be estimated from the thermal broadening of the Fermi-Dirac distribution. The oscillation amplitude is proportional to the phase coherence length $L_\phi = (D\tau_\phi)^{1/2} \sim T^{-1/2}$. In a realistic system, the impurity scattering and phonon scattering can also affect the evolution of the phase coherence with temperature. At very low temperature regime, the scattering due to paramagnetic impurity limits the increase of L_ϕ with decreasing temperature and therefore generates a saturation behavior of L_ϕ (T). At high temperature regime, the contribution of phonon scattering induces a faster decay of L_ϕ with increasing temperature than the $T^{-1/2}$ law. The temperature dependence of oscillation amplitude of the A-B oscillation in Bi₂Se₃ and Bi₂Te₃ nanowires shows a $\sim T^{-1/2}$ power law behavior from 2 K to 20 K^{37, 38}, which indicates that the electron-electron interaction is dominated in the temperature regime in their samples. In the A-B effect of Bi₂Te₃ nanoflake³⁹, the decay of oscillation with increasing temperature is faster than the $T^{-1/2}$ power law. As shown in Fig. 3.4.1(d), the decay of the FFT amplitude with increasing temperature of the β -Ag₂Te sample is compared with the $T^{-1/2}$ power law between 2 K and 10 K. There is no sign of saturation at 2 K, which shows that the impurity scattering effect is still negligible at this temperature. This may indicate the high quality of our sample. At 8 K and 10 K, it can be observed that the FFT amplitudes start deviating from the $T^{-1/2}$ law. The faster decay of FFT amplitude at 8 K and 10 K indicates the effect of inelastic phonon scattering. As the temperature dependence of the FFT amplitudes of the quantum oscillations of Bi₂Se₃ and Bi₂Te₃ nanowires agrees with the $T^{-1/2}$ power law up to 20

K, we may conclude that the phonon scattering effect is stronger in β -Ag₂Te nanoribbons than that in Bi₂Se₃ and Bi₂Te₃ nanowires.

3.5 Ambipolar electric gate effect

For a nanoribbon with topological surface states composed of Dirac cone, an ambipolar electric field effect with a sharp charge neutrality point should be expected. Pronounced ambipolar electric field effect was observed in back-gated device fabricated by a 112 nm thick β -Ag₂Te nanoribbon. Fig. 3.5.1(a) shows the back gating voltage dependent resistance curves at 2 K, 10 K, and 50 K, respectively. The gating effect is negligible when $T > 200$ K. The sharp transition at highest resistance point (the charge neutrality point) and the gradual change of resistance when the gate voltage deviates from the charge neutrality point indicate that the ambipolar behavior may be due to a Dirac cone type topological surface state. A topologically trivial surface states induced by band bending usually generates a constant highest resistance region when the Fermi level in the gap and a dramatic decrease of resistance when the Fermi level enters into the conduction band or valence band. As shown in Fig. 3.5.1(b), the sample conductance shows a quasi-linear dependence on the gating voltage in the $-20 \text{ V} < V_G < 20 \text{ V}$ regime, which also supports the topological Dirac cone origin of the surface state. It should be noted that the ambipolar electric gate effect can also be realized in semimetals or semiconductors with very narrow band gap. Although the quasi-linear gate voltage dependent conductance usually can only be observed in materials with Dirac cone surface states, we cannot fully rule out this possibility based on the current experimental results, because the possible impurity levels in the gap of β -Ag₂Te due to defects may change the narrow band semiconductor into semimetal. The resistance of the nanoribbon can change $\sim 35\%$ - $\sim 40\%$ with -60 V to 60 V gating voltage, which is a reasonable value because we can only tune the Fermi level of the bottom surface. We also observed that the highest

resistance point can shift to -50 V in a time scale of several days, which may indicate the doping effect of ambient gas to the surface states. Based on the existence of topological surface state, we also successfully explained the relationship between the shape of $R(T)$ curves and sample thickness as shown below.

Figure 3.5.1. (a) V_G dependence of resistance at 2 K, 10 K and 50 K, respectively. (b) V_G dependence of Conductance at 2 K. It shows quasi-linear behavior near the minimum conductance.

Figure 3.5.2. (a) Ambipolar field effect (4-terminals resistance R vs. V_g), measured at $T = 2$ K. The upper (lower) inset depicts a schematic cross section (optical image, top view, with the inner electrodes used to measure the voltage separated by 850 nm) of the fabricated Bi_2Te_3 device on a 500 μm -thick STO substrate. (b) Temperature (plotted in log scale) dependence of R of device measured at five gate voltages (V_g). Inset: schematic of the band diagram of Bi_2Te_3 . The horizontal dashed lines depict 3 representative locations of the Fermi energy (E_F), intercepting with the bulk conduction band (CB), topological surface states (TSS) and bulk valence band (VB), respectively. Note the Dirac point (DP) is buried inside the VB, thus only n-type TSS carriers are accessible inside the bulk bandgap. (Jauregui *et al*)⁴⁸

For comparison with our ambipolar gate effect measurements Fig. 3.5.2 and 3.5.3 are provided for other topological insulator devices, Bi_2Te_3 and $(\text{Bi}_{0.50}\text{Sb}_{0.50})_2\text{Te}_3$. For the measurement of $(\text{Bi}_{0.50}\text{Sb}_{0.50})_2\text{Te}_3$ nanoplate the sample device is ultrathin $\sim 5\text{nm}$ and the tunability that was obtained is about 50 times in Fig.3.5.3 (a) much larger than in our results Fig. 3.5.3 (a). But it is expected to observe such large ambipolar effect on ultrathin samples due to surface to volume ratio is larger in this case. In the ambipolar effect measurement performed in our next experiment presented in Chapter 4 Fig.4.2.1(d) we were able to achieve tunability of about 2500% on 98 nm thick $\beta\text{-Ag}_2\text{Te}$, which is much thicker device than $(\text{Bi}_{0.50}\text{Sb}_{0.50})_2\text{Te}_3$ nanoplate. In the Bi_2Te_3 gate effect measurement (Fig. 3.5.2(a)) were carried out on 500 μm -thick STO substrate they also observed larger ambipolar effect, more than 100%, than in our AB measurement device. Their device is also thinner compared to ours (width is 150 nm, thickness is 30 nm).

Figure 3.5.3.a, Typical dependence of resistance R on gate voltage V_G in an ultrathin $(\text{Bi}_{0.50}\text{Sb}_{0.50})_2\text{Te}_3$ nanoplate (thickness, ~ 5 nm) exhibiting a sharp peak in the resistance and subsequent decay. Inset: optical microscopy image of FET device with a thickness of ~ 5 nm as determined by AFM. **b**, High-field Hall coefficient R_H versus V_G for the same nanoplate. Each R_H (solid circle) is extracted from the Hall trace for ± 6 T at a certain V_G . At the V_G at peak R , R_H exhibits a reversal in sign. (Kong et al)⁴⁹

3.6 The shape of $R(T)$ curves vs. cross section areas

To further study the effect of topological surface state in electron transport, we also measured the temperature dependence of resistivity of $\beta\text{-Ag}_2\text{Te}$ single crystalline nanoribbons with various cross sections to find the relationship between the resistivity and cross section area. For topological insulators with the same chemical composition, due to the surface states, the resistivity should decrease with decreasing cross section at low

temperatures, which has been reported in our measurements on $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Se}_{1.8}\text{Te}_{1.2}$ bulk single crystals and nanoflake devices⁴⁴. However, we cannot figure out a clear relationship of this kind in our measurements for $\beta\text{-Ag}_2\text{Te}$ nanoribbons. We believe that this is caused by the small composition variation for different samples, which is a common problem for the CVD grown nanostructures, although the atomic ratio of Ag/Te determined by EDS is always very near 2 for all the nanoribbons measured. As $\beta\text{-Ag}_2\text{Te}$ is a narrow band semiconductor, slight composition change may generate different resistivity. The resistivity of our samples at 10 K with zero field varies from several $\text{m}\Omega\cdot\text{cm}$ to thirty $\text{m}\Omega\cdot\text{cm}$. Although there is no clear relationship between the resistivity and the area of the cross-section of samples, the shape of the resistivity vs. temperature curves does connect with the cross-section area of nanoribbons. The temperature dependence of normalized resistance of three $\beta\text{-Ag}_2\text{Te}$ nanoribbons (A, B and C) with different cross-section area is shown in Fig. 3.6.1(a), 3.6.1(b) and 3.6.1(c). The cross section areas of sample A, B and C are $6.31 \text{ width (W)} \times 0.211 \text{ thickness (T)} \mu\text{m}^2$, $1.11(\text{W}) \times 0.102 (\text{T}) \mu\text{m}^2$ and $0.191(\text{W}) \times 0.098(\text{T}) \mu\text{m}^2$, respectively. The three samples are prepared in one batch of growth. Sample A (the sample with the largest cross section area), shows semiconductor behavior in the measured temperature from 300 K to 10 K while both sample B and sample C show semiconductor characteristics at a high temperature region and present a semiconductor-to-metal transition at 50 K and 75 K, respectively. Sample C is also used for the A-B effect measurements (Fig. 3.4.1), which has the smallest cross section area. The decrease of the resistance with decreasing temperature is more pronounced in sample C comparing with that in sample B. As the A-B oscillation and ambipolar electric field effect suggests the existence of topological surface states on $\beta\text{-Ag}_2\text{Te}$, it is very natural to use the conducting surface states to account for the size dependence of electrical transport behaviors. Since the transport contribution from the metallic surface increases with decreasing size of

the sample, the metallic transport characteristic starts at higher temperatures and is more pronounced at a low temperature region.

Figure 3.6.1. The temperature dependence of normalized resistance ($\Delta\rho = \rho(T) - \rho(300\text{ K})$) at zero magnetic field of (a) sample A, (b) sample B and (c) sample C, respectively.

3.7 Conclusion

In conclusion, our first-principle calculations indicate the anisotropic topological surface state in $\beta\text{-Ag}_2\text{Te}$. Pronounced A-B oscillations and weak AAS oscillations are observed in the magnetoresistance measurements with the magnetic field applied along the current flowing direction in a single crystalline $\beta\text{-Ag}_2\text{T}$ nanoribbon, which provides an experimental evidence for the existence of the topological surface state. The ambipolar electric field effect provides further evidence of the topological surface states in $\beta\text{-Ag}_2\text{Te}$. The size dependence of the shape resistance vs. temperature curves also can be clarified by the existence of topological surface state. The experimental evidences of topological surface states and the theoretically predicted anisotropic Dirac cone suggest that $\beta\text{-Ag}_2\text{Te}$ may be a promising candidate of topological insulator for fundamental research and future spintronic devices.

Reference

1. J. E. Moore, *Nature (London)* **464**, 194 (2010).
2. M.Z. Hasan and C. L. Kane, *Rev. Mod. Phys.* **82**, 3045 (2010).
3. X. L. Qi and S. C. Zhang, *Rev. Mod. Phys.* **83**, 1057 (2011).
4. M. Konig, H. Buhmann, L. W. Molenkamp, T. L. Hughes, C. X. Liu, X. L. Qi, and S.C. Zhang, *J. Phys. Soc. Jpn.* **77**, 031007 (2008).
5. M. Konig, S. Wiedmann, C. Brune, A. Roth, H. Buhmann, L. W. Molenkamp, X. L. Qi, and S. C. Zhang, *Science* **318**, 766 (2007).
6. I. Knez, R. R. Du and G. Sullivan, *Phys. Rev. Lett.* **107**, 136603 (2011).
7. J. N. Hancock, J. L. M. van Mechelen, A. B. Kuzmenko, D. van der Marel, C. Brune, E. G. Novik, G. B. Astakhov, H. Buhmann, and L. W. Molenkamp, *Phys. Rev. Lett.* **107**, 136803 (2011).
8. C. Brune, C. X. Liu, E. G. Novik, E. M. Hankiewicz, H. Buhmann, Y. L. Chen, X. L. Qi, Z. X. Shen, S. C. Zhang, and L. W. Molenkamp, *Phys. Rev. Lett.* **106**, 126803 (2011).
9. Y. Xia, D. Dian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, *Nat. Phys.* **5**, 398 (2009).
10. Y. L. Chen, J. G. Analytis, J. H. Chu, Z. K. Liu, S. K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z. X. Shen, *Science* **325**, 178 (2009).
11. D. Hsieh, Y. Xia, L. Wray, D. Qian, A. Pal, J. H. Dil, J. Osterwalder, F. Meier, G. Bihlmayer, C. L. Kane, Y. S. Hor, R. J. Cava, and M. Z. Hasan, *Science* **323**, 919 (2009).
12. D. Hsieh, Y. Xia, D. Qian, L. Wray, J. H. Dil, F. Meier, J. Osterwalder, L. Patthey, J. G. Checkelsky, N. P. Ong, A. V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, & M. Z. Hasan, *Nature (London)* **460**, 1101 (2009).
13. J. G. Analytis, J. H. Chu, Y. Chen, F. Corredor, R. D. McDonald, Z. X. Shen, and I. R. Fisher, *Phys. Rev. B* **81**, 205407 (2010).
14. Y. S. Hor, A. Richardella, P. Roushan, Y. Xia, J. G. Checkelsky, A. Yazdani, M. Z. Hasan, N. P. Ong, and R. J. Cava, *Phys. Rev. B* **79**, 195208 (2009).
15. J. G. Checkelsky, Y. S. Hor, R. J. Cava, and N. P. Ong, *Phys. Rev. Lett.* **106**, 196801 (2011).
16. N. P. Butch, K. Kirshenbaum, P. Syers, A. B. Sushkov, G. S. Jenkins, H. D. Drew, and J. Paglione, *Phys. Rev. B* **81**, 241301(R) (2010).
17. J. Chen, H. J. Qin, F. Yang, J. Liu, T. Guan, F. M. Qu, G. H. Zhang, J. R. Shi, X. C. Xie, C. L. Yang, K. H. Wu, Y. Q. Li, and L. Lu, *Phys. Rev. Lett.* **105**, 176602 (2010).
18. H. T. He, G. Wang, T. Zhang, I. K. Sou, G. K. L. Wong, J. N. Wang, H. Z. Lu, S. Q. Shen, and F. C. Zhang, *Phys. Rev. Lett.* **106**, 166805 (2011).
19. S. Matsuo, T. Koyama, K. Shimamura, T. Arakawa, Y. Nishihara, D. Chiba, K. Kobayashi, T. Ono, C. Z. Chang, K. He, X. C. Ma, and Q. K. Xue, *Phys. Rev. B* **85**, 075440 (2012).
20. J. Wang, A. M. DaSilva, C. Z. Chang, K. He, J. K. Jain, N. Samarth, X. C. Ma, Q. K. Xue, and M. H. W. Chan, *Phys. Rev. B* **83**, 245438 (2011).
21. R. Xu, A. Husmann, T. F. Rosenbaum, M. L. Saboungi, J. E. Enderby, and P. B. Littlewood, *Nature (London)* **390**, 57 (1997).
22. A. Husmann, J. B. Betts, G. S. Boebinger, A. Migliori, T. F. Rosenbaum, and Saboungi M. L. *Nature (London)* **417**, 421 (2002).
23. A. A. Abrikosov, *Phys. Rev. B* **58**, 2788 (1998).
24. M. M. Parish, and P. B. Littlewood, *Nature (London)* **426**, 162 (2003).
25. J. S. Hu and T. F. Rosenbaum, *Nat. Mater.* **7**, 697-700 (2008).

26. W. Zhang, R. Yu, W. X. Feng, Y. G. Yao, H. M. Weng, X. Dai, & Z. Fang, *Phys. Rev. Lett.* **106**, 156808 (2011).
27. V. E. Sacksteder IV, S. Kettemann, X. Dai, Q. S. Wu, and Z. Fang, arXiv:11082938v1, (2011).
28. G. Kresse, and J. Hafner, *Phys. Rev. B* **48**, 13115 (1993).
29. P. E. Blochl, *Phys. Rev. B* **50**, 17953-17979 (1994).
30. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865-3868 (1996).
31. D. D. Koelling, and B. N. Harmon, *J. Phys. C: Solid Stat. Phys.* **10**, 3107 (1977).
32. A. van der Lee, and J. L. de Boer, *Acta Cryst.* **C49**, 1444-1446 (1993).
33. R. Dalven, *Phys. Rev. Lett.* **16**, 311-312 (1966).
34. R. Dalven and R. Gill, *Phys. Rev. B* **159**, 645-649 (1967).
35. L. Fu, *Phys. Rev. Lett.* **103**, 266801 (2009).
36. J. H. In, Y. D. Yoo, J. G. Kim, K. Y. Seo, H. J. Kim, H. Ihee, S. H. Oh, and B. S. Kim, *Nano Lett.* **10**, 4501 (2010).
37. H. Peng, K. Lai, D. Kong, S. Meister, Y. Chen, X.-L. Qi, S.-C. Zhang, Z.-X. Shen, and Y. Cui *Nat. Mater.* **9**, 225 (2010).
38. F. X. Xiu, L. He, Y. Wang, L. Cheng, L. T. Chang, M. Lang, G. Huang, X. F. Kou, Y. Zhou, X. W. Jiang, Z. G. Chen, J. Zou, A. Shailos, and K. L. Wang, *Nat. Nano.* **6**, 216 (2011).
39. Z. G. Li, Y. Y. Qin, F. Q. Song, Q. H. Wang, X. F. Wang, B. G. Wang, H. F. Ding, C. van Haesdonck, J. G. Wang, Y. H. Zhang, G. H. Wang, *Appl. Phys. Lett.* **100**, 083107 (2012).
40. Y. Zhang, and A. Vishwanath, *Phys. Rev. Lett.* **105**, 206601 (2010).
41. J. H. Bardarson, P. W. Brouwer, and J. E. Moore, *Phys. Rev. Lett.* **105**, 156803 (2010).
42. T. Richer, C. Blomers, H. Luth, R. Calarco, M. Indlekofer, M. Marso, and T. Schapers, *Nano Lett.* **8**, 2834 (2008).
43. C. Y. Moon, J. H. Han, H. Lee, and H. J. Choi, *Phys. Rev. B* **84**, 195425 (2011)
44. B. Xia, P. Ren, A. Sulaev, P. Liu, S.-Q. Shen, L. Wang, arXiv:1203:2007v4
45. V. F. Gantmakher, *Electrons and Disorder in Solids*, Oxford Science Publications, 2005
46. S.G. Lee, J.H. In, Y.D. Yoo, Y.G. Jo, Y. C. Park, H. J. Kim, H. C. Koo, J. Kim, B. S. Kim, and K. L. Wang, *Nano Lett.* **12**, 4194 (2012)
47. H. Steinberg, D. R. Gardner, Y. S. Lee, and P. J. Harillo, *Nano Lett.* **10**, 5032 (2010)
48. L. A. Jauregui, M. T. Pettes, L. P. Pokhinson, L. Shi, and Y. P. Chen, *Sci. Rep.* **5**, 8452 (2015)
49. D. Kong, Y. Chen, J. J. Cha, Q. Zhang, J. G. Analytis, K. Lai, Z. Liu, S. S. Hong, K. J. Koski, S. K. Mo, Z. Hussain, I. R. Fisher, Z. X. Shen, and Y. Cui, *Nat. Nano.* **6**, 705 (2011)

Chapter 4. Gate-tuned quantum oscillations of topological surface states in β -Ag₂Te

Further electrical measurements were performed on the β -Ag₂Te nanowires and nanoplates. In the following chapter we report the first experimental confirmation of the existence of topological surface states with high electric field tunability and mobility in β -Ag₂Te. The first experimental results presented will differentiate Ag₂Te nanoplate and nanowire temperature and gate voltage dependences. Then Shubnikov-de Haas (SdH) oscillations obtained in Ag₂Te nanoplate and nanowire will be analyzed.

4.1. Introduction

In the previous chapter the Aharonov-Bohm quantum oscillations obtained clearly indicate the topological nature of the β -Ag₂Te material. But in order to explore the possible application of TI in spintronics, ideal TI systems are expected to exhibit high mobility and gate electric field tunability. Since the first experimental realization of TI in CdTe/HgTe/CdTe quantum well structures⁵, an extensive effort has been put up in search for new TI systems. To date, CdTe/HgTe/CdTe⁵ and InAs/GaSb⁶ have been experimentally confirmed to be two-dimensional TIs while strained HgTe and many Bi based compounds such as Bi_xSb_{1-x}, Bi₂Se₃ and Bi₂Te₃ have been realized as three-dimensional TIs.⁸⁻²⁴ To explore the possible application of TI in spintronics, ideal TI systems are expected to exhibit high mobility and gate electric field tunability. However, most of the TI materials show very small surface contribution due to defect-induced large bulk contribution and therefore electric field tunability cannot be realized. On the other hand, very few TIs that manifest electric field

ambipolar effect such as $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ ^{27, 28, 29} and thin Bi_2Se_3 flakes^{21, 25}, show low mobility. On this basis, it is important to identify new TIs that show large gate electric field tunability and high surface mobility for the application of future TI based spintronic devices.

The $\beta\text{-Ag}_2\text{Te}$ is known for its unusual large and non-saturating quasi-linear magnetoresistance (MR) in the field range of $10\text{-}10^5$ Oe and temperature range of $5\text{-}300$ K³⁰⁻³². The origin of this unusual property has generated much debate since its discovery and may be associated with its 3D-TI nature. Theoretical calculation suggests that $\beta\text{-Ag}_2\text{Te}$ is a TI with anisotropy and the unusual MR is largely originated from electrical transport on the topological surface states³³. Recently, Aharonov-Bohm (AB) oscillations have been observed in a nanowire of $\beta\text{-Ag}_2\text{Te}$ which indicates the existence of surface states^{34, 35}. However, the topological nature of the surface state still remains to be confirmed.

In this work, we provide further experimental evidence of the existence of topological surface states in $\beta\text{-Ag}_2\text{Te}$. Especially, the topological surface state of narrow Ag_2Te nanoplate exhibits the largest electric field ambipolar effect in TI so far ($\sim 2500\%$). We fabricated nanoplate devices as shown in the inset of Fig. 4.2.1(a) and Fig. 4.2.1(b). Both devices show pronounced two dimensional (2D) SdH oscillations. Using the measured resistivity ρ_{xx} and Hall resistivity ρ_{xy} of the wide nanoplate as shown in Fig. 1(a), the conductivity σ_{xx} is calculated and the Berry phase is determined to be near π by Landau Level (LL) fan diagram. This reveals that the SdH oscillation originates from the topological surface states. Utilizing the large ambipolar field effect of the narrow nanoplate as shown in Fig. 4.2.1(b), the evolution of SdH oscillations with applied gate voltage (V_g) was investigated and also strongly indicates a Dirac cone composed surface state. Moreover, the mobility of the surface transport of the narrow $\beta\text{-Ag}_2\text{Te}$ nanoplate is determined to be several

thousand $\text{cm}^2\text{s}^{-1}\text{V}^{-1}$. Finally, the MR variation with V_g of the narrow nanoplate indicates a correlation effect between the bulk electrons and Dirac fermions.

4.2. Temperature and gate voltage dependence

The typical transport behavior of two devices fabricated from a relatively wide nanoplate and a narrow nanoplate grown by CVD methods are shown in Fig. 4.2.1(a)-(d). It should be emphasized that similar results have been repeated in several devices fabricated using wide and narrow nanoplates. The wide $\beta\text{-Ag}_2\text{Te}$ nanoplates tend to be slightly n-type. The inset of Fig. 4.2.1(a) and Fig. 4.2.1(b) show the fabricated devices using heavily p-doped Si with 300nm thick of SiO_2 dielectric layer. The thicknesses and widths for the two nanoplate devices are 120 nm (thickness), 5 μm (width) and 98 nm (thickness), 395 nm (width), respectively. As shown in Fig. 4.2.1(a), the resistance (R_{xx}) of the relatively wide nanoplate decreases slightly with temperature from $T = 300$ K to 250 K, then increases about several times from 250 K to 30 K, and finally decreases to 10 K.

The special temperature dependence of R_{xx} of the nanoplate is due to the light impurity doping, which has been observed in many doped semiconductor systems³⁶. The metallic behavior at low temperature of the nanoplate is attributed to the conduction in the impurity band, while the metallic behavior when $T > 250$ K can be explained by the thermal excitation of electrons from the Anderson localized states to extended states above the mobility edge. A better stoichiometry is achieved in the narrow nanoplate, and hence we observed much sharper increase of resistance with decreasing temperature as shown in Fig. 4.2.1(b). The gradually saturating behavior at low temperatures is due to the surface states. To probe the existence of surface states, we have performed the gate-tuned resistance measurement. As shown in Fig. 4.2.1(c), the R_{xx} of the wide nanoplate only changes slightly with V_g in view of electron doping. Although the V_g dependence of R_{xx} shows a peak near 0 V, the voltage

dependence of Hall resistance (R_{xy}) and SdH oscillations indicates that electric field ambipolar gate effect cannot be realized in wide nanoplate devices due to charge doping.

The resistance change with an applied gate voltage may originate from the variation of the density of states at the Fermi level in the bulk states when the Fermi level is slightly shifted by the gate electric field. We observed the phenomenon in several wide nanoplate samples. In contrast to wide nanoplates, the narrow nanoplates shows a huge ambipolar type electric field effect under a back V_g , which further confirms the high stoichiometry as indicated by the temperature dependence of resistivity curve. Fig. 4.2.1(d) shows that the gate induced resistance change ($R_{\text{peak}}/R_{+50 \text{ V}}$) in the narrow $\beta\text{-Ag}_2\text{Te}$ nanoplate is $\sim 2500\%$, a value which is much larger than that obtained in any other TIs. Here, the R_{peak} and $R_{+50 \text{ V}}$ is the resistance at the peak of the ambipolar curve and $V_g = +50 \text{ V}$, respectively. The sharp transition at highest resistance point (the charge neutrality point) and the gradual change of resistance when the V_g deviates from the charge neutrality point indicate that the ambipolar behavior could be due to topological surface states of Dirac cone. However, it should be emphasized that the ambipolar electric field effect can also be realized in semimetal or semiconductor with a very narrow band gap. In order to probe the topological nature of the surface state, we have performed two experiments. We first determine the Berry phase from the SdH oscillation of the conductivity of the wide nanoplate and then investigate the evolution of SdH oscillation with V_g since the narrow nanoplate shows huge V_g dependence of resistance of Dirac cone type.

Figure 4.2.1. Temperature and voltage dependence of resistance. (a) and (b) show the temperature dependence of resistance of β -Ag₂Te wide and narrow nanoplates, respectively. The insets show the corresponding device images. The red bars are 5 μ m and 10 μ m in (a) and (b), respectively. The arrow in (b) points to the narrow nanoplates. (c) and (d) show the V_g dependence of resistance of β -Ag₂Te at 2 K.

4.3. Berry phase obtained from SdH oscillations.

Figure 4.3.1(a) shows the R_{xy} of the wide nanoplate device under tilted magnetic field (B) as a function of the component of the magnetic field perpendicular to the sample surface ($B_{\perp}$). The angle (θ) is defined between the B field and sample surface. The R_{xy} indicates an n-type carrier and a clear deviation from the linear relationship with B field. This demonstrates that

there are more than one transport channel with different mobility values. At higher field, the R_{xy} oscillates periodically in $1/B$, which is the standard behavior of SdH oscillation. More importantly, we observe that the positions of maxima and minima do not change with $B_{\perp}$ field. As you can see in Fig.4.3.3 (a) for Bi_2Te_3 the SdH oscillations also do not change with $B_{\perp}$, as shown by the blue line connecting the squares representing the same peak at $B_{\perp}$. This clearly indicates that the oscillations originate from 2D transport behavior. No oscillations are observed in R_{xx} vs B curve (not shown here) when the applied magnetic field is parallel to the sample surface, which further supports the 2D transport and rules out the oscillation from bulk in this sample. The lack of the SdH oscillations from bulk electrons indicates low mobility of the bulk transport in this device.

A prominent property of Dirac fermions is that they carry the Berry phase of π . The observation of a π phase shift in SdH oscillation would clearly demonstrate that the 2D transport is indeed due to the topological surface transport^{4, 37}. SdH oscillations originate from successive emptying of Landau Levels (LL) with increasing magnetic field. The LL index n is related to the cross section area S_F of the Fermi surface by

$$2\pi(n + \gamma) = S_F \frac{\hbar}{eB} \quad (4.3.1)$$

where $\gamma = 0$ or $1/2$ for topological trivial electrons and Dirac Fermions, respectively, e is the electron charge, $\hbar$ is the Planck constant ($\hbar = \frac{h}{2\pi}$), and B is the magnetic flux density. Fig.

4.3.1(b) is the R_{xy} and R_{xx} of the wide nanoplate with a storage in vacuum for three days after the measurement in Fig 4.3.1(a). As shown in Fig. 4.3.1(b), the SdH oscillation of R_{xy} changes after the storage in vacuum, which indicates the doping of surface or bulk states. To obtain the value of Berry phase of the system, we calculate the conductivity using the formula $\sigma_{xx} = \rho_{xx}/(\rho_{xx}^2 + \rho_{xy}^2)$ for both measurements in Fig 4.3.1 (a) and Fig 4.3.1 (b). Thereafter the

$\Delta\sigma_{xx}$ is obtained through a smooth background subtraction. The $\Delta\sigma_{xx}$ vs $1/B$ curves for both conditions show oscillations of a single period which indicates only one transport channel in the surface states of the sample contributing to the oscillations. The inset of Fig. 4.3.1 (c) is the $\Delta\sigma_{xx}$ vs $1/B$ curve obtained from Fig. 4.3.1 (b). The LL fan diagrams based on the oscillations of the conductivity for both situation are shown in Fig. 4.3.1 (c), where their minima are identified to signify the integer n (indicated by arrows), while the half integers $n+1/2$ are assigned to the positions of maxima (indicated by arrows). The interception at $1/B = 0$ should be at $n = 0$ (for the topological trivial surface states) or $n = 1/2$ (for the topological surface states). As shown in Fig. 4.3.1 (c), linear fits to the data give interception of 0.52 (the blue fitting line) and 0.54 (the red fitting line) for the sample before the storage and after the storage, respectively. The values are close to the value of 0.5 expected for Dirac fermions. In the Fig.4.3.3 (d) similar Landau Level index diagram derived from SdH oscillations is plotted for Bi_2Te_3 device. In their measurement the intersection is at -0.5, although if we shift LL indexing by 1 then the intersection will be at 0.5.⁴² This result strongly supports that the SdH oscillation is indeed originated from the topological surface states. The doping due to the storage can shifts the Fermi level, but it does not change the topological characteristics.

Figure 4.3.1. SdH oscillations and fan diagram analysis. (a) Hall resistance (R_{xy}) as a function of the B field measured at various tilted angles (q); (b) R_{xx} and R_{xy} as functions of the B field with $q = 90^\circ$. The measurements were performed using the same sample for (a), which had been stored for three days in vacuum after the measurements in (a); (c), SdH fan diagrams for measured $1/B$ with the filling factor n . The blue and red data and fitting lines are for the device before the storage and after the storage, respectively. The squares and circles are the maxima and minima, respectively. The inset shows the ΔR_{xx} vs. $1/B$ plot for the device after the storage; (d) R_{xx} vs. B field curves at various temperatures. The inset shows the SdH oscillation after subtracting the background MR. (e) The temperature dependence of relative amplitude of SdH oscillation in $\Delta R_{xx}(B)$ for the 3rd LL. The solid line is a fit to $\frac{\alpha T / \Delta E_N(B)}{\sinh[\alpha T / \Delta E_N(B)]}$; (f) $\ln(\Delta R_B \sinh(\alpha T / \Delta E_N))$ is plotted as a function of $1/B$.

Figure 4.3.2. SdH oscillations in Bi_2Se_3 (a) $\Delta R_{xx}(B)$, extracted from $R_{xx}(B)$ by subtracting a smooth background, at various temperatures (T). Arrows label selected LL indices. (b) T dependence of the relative amplitude of SdH oscillation in $\Delta R_{xx}(B)$ for the 10th LL. The solid line is a fit to the Lifshitz-Kosevich formula, from which we extract LL energy gap ΔE . The inset shows ΔE as a function of B (magnetic field positions of minima in R_{xx} corresponding to different LLs), and the effective mass ($m^* \sim 0.14m_e$) is extracted from the slope of the linear fitting. (c) $\ln[D]$ (defined in the text) plotted as a function of $1/B$. The Dingle temperature $T_D = 25$ K is calculated from the slope of the linear fit, corresponding to a carrier lifetime $\sim 5 \times 10^{14}$ s and an effective mobility of $\sim 620 \text{ cm}^2/\text{V s}$. (Cao *et al*)¹⁶

Figure 4.3.4 (a) Angle dependence of the Shubnikov–de Haas oscillations for 200 nm thick Bi_2Te_3 , at 4.2 K, (top to bottom: the angle between the magnetic field and the surface normal $\phi = 0^\circ$ – 60° in steps of 10°) after subtraction of a linear background. The square markers represent the expected shift of the maxima in magnetic field for a 2D system, given by $B_\perp = B\cos(\phi)$, indicating that the oscillations arise from surface states. (b) Oscillation amplitude dependence on the magnetic field (minima as black squares and maxima as red circles); linear backgrounds have been subtracted, leaving the oscillating part. We deduce a Dingle temperature $T_D = 1.65$ K from fitting the increase in oscillation amplitude with increasing field. Only the magnetoresistance in small fields is considered, where the peak splitting is negligible. (c) Oscillation amplitude dependence on temperature; linear backgrounds have been subtracted. The effective mass $m^* = 0.16 m_0$ is estimated by fitting the decrease of the magnetoresistance oscillations as function of temperature (peaks at least up to 9 T in both the conductance and resistance result in the same effective mass). (d) The $1/B$ values versus the Landau level index n intersect at $n = -0.5$, consistent with a half-filled lowest Landau level, as expected for a Dirac cone. (Veldhorst et al)⁴²

Figure 4.3.1(d) displays the temperature dependence of SdH oscillations of R_{xx} . The inset shows the ΔR_{xx} obtained from R_{xx} by subtracting a polynomial fit to the background. The amplitude of the SdH oscillations decreases with increasing temperature due to thermal agitation of electrons on the Landau levels. We have used the standard Lifshitz-Kosevich theory

$$\Delta R_{xx}(T, B) \propto \frac{\alpha T / \Delta E_N(B)}{\sinh[\alpha T / \Delta E_N(B)]} e^{-\alpha T_D / \Delta E_N(B)} \quad (4.3.2)$$

to fit the temperature dependence of SdH oscillations, where $\Delta E_N = \hbar e B / 2\pi m^* c$ is the energy gap between Nth and (N+1)th Landau Level, $T_D = \hbar / 4\pi^2 k_B$ is the Dingle temperature, and $\alpha = 2\pi^2 k_B$. The B , $\hbar$, m^* , k_B , and c are the magnetic field, Planck constant, the effective mass of carriers, Boltzmann constant, and speed of light, respectively. The temperature dependence of $\Delta R / \Delta R(0 \text{ K})$ for the 3rd Landau level is plotted in Fig. 4.3.1(e).

The solid line is a fit to $\frac{\alpha T / \Delta E_N(B)}{\sinh[\alpha T / \Delta E_N(B)]}$. The $\Delta R(0 \text{ K})$ is the ΔR at 0 K obtained from the fitting and m^* can be calculated using the fitted value of E_N . We averaged the value obtained for different B to get $m^* = 0.12m_e$. In comparisons the m^* values obtained for Bi_2Se_3 (Fig.4.3.2 (b)) and Bi_2Te_3 (Fig.4.3.3(e)) are $0.14m_e$ and $0.16 m_e$ respectively. From the slope of the semi-log plot of $\Delta R B \sinh(\alpha T / \Delta E_N)$ vs $1/B$ at $T = 2 \text{ K}$, the T_D is determined to be 13.6 K (Bi_2Se_3 : $T_D = 25 \text{ K}$, Bi_2Te_3 : $T_D = 1.65 \text{ K}$) and the carrier life-time is calculated to be $8.9 \times 10^{-14} \text{ s}$. The mobility is then determined to be $1310 \text{ cm}^2\text{s}^{-1}\text{V}^{-1}$, which is higher than in Bi_2Se_3 device ($620 \text{ cm}^2\text{s}^{-1}\text{V}^{-1}$) but lower than in Bi_2Te_3 device ($8300 \text{ cm}^2\text{s}^{-1}\text{V}^{-1}$).^{16,42}

4.4. SdH oscillations with gate

The existence of Dirac cone composed topological surface states can be further investigated by examining the evolution of the SdH oscillation in the narrow nanoplate through back gating. From Eq. (4.3.1), we know that the period of R_{xx} vs $1/B$ is determined by the cross section of Fermi surface as shown in Eq. (4.4.1),

$$\Delta \frac{1}{B} = \frac{2\pi e}{\hbar S_F} \quad (4.4.1)$$

Assuming a circular 2D Fermi surface or a spherical 3D Fermi surface, the value of Fermi wave vector k_F can be calculated using $S_F = \pi k_F^2$. Thereafter, the carrier density of 2D

surface states and 3D bulk states can be calculated by $n_{2D} = \frac{k_F^2}{2\pi}$ and $n_{3D} = \frac{k_F^3}{3\pi^2}$, respectively.

The dependence of R_{xx} on B field under various V_g was performed and the results are shown in Fig. 4.4.1(a)-(h). To analyze the SdH oscillations, ΔR_{xx} is obtained from R_{xx} by subtracting a polynomial fit to the background. The ΔR_{xx} vs $1/B$ curves with various V_g s are shown in Fig. 4.4.1 (a)-(f). The curves at -12 V and -50 V do not show reasonable SdH oscillations, which may contribute to the very small Fermi surface and large noise, respectively. From Fig. 4.4.1, it is clearly evident that the period of SdH oscillation rises when V_g varies from +50 V to -8 V. This demonstrates that the area of Fermi surface decreases when V_g changes from +50 V to -8 V. With further increasing amplitude of V_g to the negative direction, the magnitude of SdH oscillations gradually diminishes.

Figure 4.4.1. R_{xx} of the narrow plate as a function of B field measured under various V_g , (a) +50 V, (b) +25 V, (c) +10 V, (d) 0 V, (e) -8 V, (f) -12 V, (g) -25 V and (h) -50 V.

Figure 4.4.2 (a–f) Shubnikov–de Haas oscillations in Bi_2Te_3 at different temperatures and gate voltages. The oscillations become more pronounced as the gate voltage increases from -60 V to $+80$ V at $T = 1.4$ K (a) and 4 K (d). Purple arrows in the corresponding FFT spectra (b,e) indicate the frequency of the SdH oscillations, which represent the surface states. Green solid dots suggest the presence of other oscillation frequencies, which are developed when the bulk carrier concentration increases under negative gate voltages. The oscillations also become more pronounced as the temperature decreases from 8 K to 1.4 K at gate voltages of $+80$ V (c) and $+40$ V (f). (g), Normalized conductivity amplitude versus temperature at gate voltages of $+80$ V and $+40$ V. A magnetic field of 7.4 T was used to extract the cyclotron effective mass: $\sim 0.131m_0$ ($+80$ V) and $\sim 0.119m_0$ ($+40$ V). (h,i) Dingle plots at three different temperatures at gate voltages of $+80$ V (h) and $+40$ V (i). Transport lifetime, mean free path and mobility can be extracted from the best fit to $\log [(\Delta R/R_0)B \sinh \lambda]$. (Xiu *et al*)⁴²

The SdH oscillations can still be clearly observed and the period of the oscillations decreases when V_g varies from -8 V to -25 V. This demonstrates that the area of Fermi surface increases in the procedure. This correlates well with the scenario that the area of the Fermi surface increases with the Fermi level shifting away from the Dirac point. In order to understand the band structure of β -Ag₂Te, we fit the ΔR_{xx} vs $1/B$ curve with the theoretical expression for SdH oscillations. The formula can be written as

$$\Delta R_{xx} = A \exp(-\pi / \mu B) \cos[2\pi(B_F / B + 1/2 + \beta)] \quad (4.4.2)$$

where B_F is the frequency of the SdH oscillation, A is the amplitude, μ is the mobility of carriers, and β is the Berry phase^{22, 23}. Equation (4.4.3) is in fact a zero temperature formula, which considers the effect of finite relaxation time but ignores the temperature effect³⁸. As the accurate phase analysis should use the value of conductivity $\sigma_{xx} = \rho_{xx}/(\rho_{xx}^2 + \rho_{xy}^2)$, especially for systems like β -Ag₂Te that has similar values of ρ_{xx} and ρ_{xy} , the β value obtained in the fitting to ΔR_{xx} cannot provide the information of topological nature⁴. Here, we focus on two fitting parameters, the B_F and μ . The experimental data (red circles) and fitting curves (green lines) are shown in Fig. 4.4.3. In the fitting process, the B_F values are first roughly determined by inspection and FFT transformation. Thereafter, accurate B_F s and μ s are fitted. Three transport channels are employed to fit the SdH oscillations at $V_g = +50$ V and $V_g = +25$ V. One transport channel is utilized to fit the oscillations at other applied V_g s. The SdH oscillations at -8 V (Fig. 4.4.3(e)) show an abrupt increase at the large field, which probably originates from the deviation of background subtraction. A large deviation at large field can appear when the number of oscillations is small. The phase deviation of the fitting at large field ($1/B < 0.15 \text{ T}^{-1}$ or $B > 6.7 \text{ T}$) at -25 V (Fig. 4.4.3(f)) may result from the large noise of the data and error in background subtraction. The three peaks and three valleys in low field

range of $0.15 \text{ T}^{-1} < 1/B < 0.25 \text{ T}^{-1}$ clearly indicates a larger oscillation period compared with that at $V_g = 0 \text{ V}$ and -8 V .

Figure 4.4.3. ΔR_{xx} as a function of $1/B$ field with various V_g . (a) +50 V, (b) +25 V, (c) +10 V, (d) 0 V, (e) -8 V, (f) -25 V. The red circles are the experimental data. The green lines are the fitting curves.

	B_F (T)	μ ($\times 10^3 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$)	k_F ($\times 10^{-2} \text{ \AA}^{-1}$)
+50 V	83.5 ± 0.5	2.1 ± 0.2	5.04 ± 0.02
	70.5 ± 0.5	1.5 ± 0.2	4.63 ± 0.02
	45.6 ± 0.5	1.4 ± 0.2	3.72 ± 0.02
+25 V	52 ± 0.5	2 ± 0.2	3.98 ± 0.02
	44.1 ± 0.5	2 ± 0.2	3.67 ± 0.02
	10.6 ± 0.5	2.5 ± 0.2	1.80 ± 0.02
+10 V	24 ± 2	1 ± 0.2	2.70 ± 0.1
0 V	14.1 ± 2	4 ± 0.5	2.07 ± 0.2
-8 V	10.2 ± 2.5	30 ± 5	1.75 ± 0.4
-25 V	25.1 ± 1	2 ± 0.3	2.76 ± 0.06

Table 1 | The fitting parameter B_F and m for SdH oscillations, and the calculated k_F from the fitted B_F at various V_{gS} .

Although the fittings deviate in some features, our fitting do reveal the main features of the experimental data. The fitted B_F s and μ s are shown in table 1. Based on the B_F values, the values of k_F s are calculated as listed in the table. The V_g dependence of k_F is depicted in Fig. 4.4.4(a), in which both the negative and positive value of k_F is plotted as the red squares. For the SdH at +50 V and +25 V, we choose the largest B_F to calculate the k_F . The green dashed line is drawn to clearly depict the cone structure. As previously discussed, the ambipolar effect can originate from the topological surface or bulk state of a semimetal. For the same Fermi surface area perpendicular to B field, the bulk state has a much larger carrier density. Using the formulae as aforementioned, the calculated carrier densities at +50 V are $n_{3D} = 4.3 \times 10^{18} \text{ cm}^{-3}$ for the bulk state of semimetal and $n_{2D} = 4.0 \times 10^{12} \text{ cm}^{-2}$ for the Dirac cone composed surface state. At 0 V, the corresponding values for n_{3D} and n_{2D} are $3.0 \times 10^{17} \text{ cm}^{-3}$ and $6.8 \times 10^{11} \text{ cm}^{-2}$, respectively. We note that the charge tunability of a 300 nm SiO_2 dielectric layer is about $3.6 \times 10^{12} \text{ cm}^{-2}/50 \text{ V}$. Considering the sample thickness of 98 nm, if the ambipolar behavior was due to the bulk state, the tuned charge would be $4.2 \times 10^{13} \text{ cm}^{-2}$ which is 11 times larger than the tuning ability of a SiO_2 dielectric layer. Thus, our results clearly rule out the possibility of bulk originated ambipolar behavior and provide further strong evidence of the existence of surface states of Dirac cone type. As for the other two channels showing SdH oscillations at $V_g = +50 \text{ V}$ and $+25 \text{ V}$, we speculate that they originate from the Rashba splitting induced topological trivial surface states, which have shown by the Altshuler-Aronov-Spivak oscillations in the $\beta\text{-Ag}_2\text{Te}$ nanowire³⁴.

Figure 4.4.4. V_g dependence of k_F and μ . (a) The variation of k_F with V_g . Plotted k_F values are $\pm k_F$. The red squares are the calculated results based on the SdH oscillations. The green lines are plotted to depict the cone structure. (b) The V_g dependence of the carrier mobility μ .

The V_g dependence of the mobility is shown in Fig. 4.4.4(b), the carrier mobility is in the range between $\sim 1 \times 10^3$ to $\sim 2 \times 10^3 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ when the gate voltage varies from +50 V to +10 V. It increases to $\sim 4 \times 10^3 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ at $V_g = 0$ V and then the mobility decreases to $\sim 2 \times 10^3 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ at $V_g = -25$ V. The obtained mobility values are decent compared with that in other topological insulators^{11, 19-21, 38, 40}. It also agrees with the mobility value ($1310 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$) obtained for the doped β - Ag_2Te nanoplate. The shape of the oscillations at -8 V is different from that of the standard SdH oscillation, which indicates a large artefact from subtraction. Because the fitted value of μ is closely related to the shape of the SdH oscillation (the decay of the oscillation amplitude), the very large mobility value ($3 \times 10^4 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ as shown in table 1) at $V_g = -8$ V is probably not reliable. Using the width of the narrow nanoplate (395

nm) and the interval between the contact (7.2 μm), we can calculate the sheet resistance and then calculate the mobility using $\mu = \sigma/en$. Considering the devices have top and bottom surfaces, the calculated mobility at $V_g = 0$ is $\sim 5 \times 10^3 \text{ cm}^2\text{s}^{-1}\text{V}^{-1}$, which also agrees well with the result obtained from SdH oscillation. For V_g s very near the charge neutrality point, we cannot get accurate k_F due to the lacking of enough oscillations. The variation of MR with V_g in the low field regime also shows an interesting feature. As depicted in Fig. 4.4.1(d), (e), (f), the MR presents a relatively sharp increase in the low field regime (circled by green dash lines) at $V_g = 0 \text{ V}$, -8 V and -12 V , near the charge neutrality point and does not appear in the MR curves under other applied V_g . This may suggest that the π Berry phase induced weak anti-localization can be manifested when the E_F is far away from the bulk band. In all, it is strongly indicated that $\beta\text{-Ag}_2\text{Te}$ is a TI from the Berry phase of π obtained from LL fan diagram as shown in Fig. 4.3.1(c) and Dirac cone type evolution of SdH oscillations under V_g as depicted in Fig. 4.4.1, 4.4.3, 4.4.4

4.5. The voltage dependence of MR

As aforementioned, the origin of the unusual MR of $\beta\text{-Ag}_2\text{Te}$ is still under debate, which may originate from the bulk effect or surface effect²⁸⁻³². To distinguish the bulk from the surface effect, high quality samples with tunable Fermi level are indispensable. It has not been realized prior to this work. Figure 4.4.5 shows the comparison of ambipolar effect and MR under applied V_g . The MR is defined as $(R(9 \text{ T}) - R(0 \text{ T}))/R(0 \text{ T})$, which depicts a clear correlation with the E_F position. The MR displays a lowest value of 78% at V_g of the charge neutrality point. When the V_g deviates from the charge neutrality point, the MR gradually increases in both negative and positive directions and reaches a maximum value at the voltages when the electric field ambipolar effect saturates. Thereafter, the resistance

decreases with increasing V_g magnitude in both negative and positive directions. Based on the relationship between the E_F position and electric field ambipolar curve, we can clearly describe the MR behavior in β -Ag₂Te. At the charge neutrality point, the E_F is located at the Dirac point and MR presents the lowest value. When the E_F in the bulk band gap (but on the Dirac type surface states) is moved to the conduction band or valence band, the MR increases continuously until the E_F touches the bulk band. Thereafter, any further manipulation to the bulk causes MR to decrease. Other than the bulk or surface origin of large quasi-linear MR, our experiment provides the possibility of controlling the interplay of bulk and topological surface state⁴¹. As shown in Fig. 4.4.3, the gated MR demonstrates that the largest MR appears near the top of the valence band and bottom of the conduction band, where the bulk electrons and Dirac Fermions can have a strong correlation. We still do not fully understand the correlation effect between the bulk electrons and Dirac Fermions, which deserves further theoretical and experimental investigations.

Figure 4.4.5. The MR measured under various applied V_g . The R_{xx} vs V_g curve is plotted for comparison.

4.6. Conclusion

In conclusion, using LL fan diagram obtained from the oscillation of σ_{xx} and the variation in the period of SdH oscillation with applied V_g , we provide strong evidence of the topological nature of surface states in β -Ag₂Te. The topological surface states of highly stoichiometric narrow β -Ag₂Te nanoplate exhibit the largest ambipolar effect in TI so far (~2500 %) and decent mobility (a few thousand $\text{cm}^2\text{s}^{-1}\text{V}^{-1}$). This indicates that β -Ag₂Te has the potential to become an important material for TI investigation. Moreover, the first report of V_g dependence of MR in β -Ag₂Te suggests that the interplay between the bulk electrons and surface Dirac fermions has a large effect on MR for this material.

References

1. J. E. Moore, *Nature* **464**, 194–198 (2010)
2. X. L. Qi, and S.C. Zhang, *Phys. Today* **63**, 33 (2010)
3. M. Z. Hasan, and C. L. Kane, *Rev. Mod. Phys.* **82**, 3045–3067 (2010)
4. Y. Ando, *J. Phys. Soc. Jpn.* **82**, 102001 (2013)
5. M. König, *et al*, *Science* **318**, 766–770 (2007)
6. I. Knez, R. R. Du, and G. Sullivan, *Phys. Rev. Lett.* **107**, 136603 (2011)
7. J.N. Hancock, *et al*, *Phys. Rev. Lett.* **107**, 136803 (2011)
8. J. G. Checkelsky, Y. S. Hor, R. J. Cava, and N. P. Ong, *Phys. Rev. Lett.* **106**, 196801 (2011)
9. J. G. Checkelsky, *et al*, *Phys. Rev. Lett.* **103**, 246601 (2009)
10. N. P. Butch, *et al*, *Phys. Rev. B* **81**, 241301 (2010)
11. D. X. Qu, Y. S. Hor, J. Xiong, R. J. Cava, and N. P. Ong, *Science* **329**, 821–824 (2010)
12. H. Peng, *et al*, *Nat. Mater.* **9**, 225–229 (2010)
13. J. Chen, *et al*, *Phys. Rev. Lett.* **105**, 176602 (2010)
14. Y. S. Kim, *et al*, *Phys. Rev. B* **84**, 073109 (2011)
15. M. Liu, *et al*, *Phys. Rev. Lett.* **108**, 036805 (2012)
16. H. L. Cao, *et al*, *Phys. Rev. Lett.* **108**, 216803 (2012)
17. H. T. He, *et al*, *Phys. Rev. Lett.* **106**, 166805 (2011)
18. H. Steinberg, D. R. Gardner, Y. S. Lee, and P. Jarillo-Herrero, *Nano Lett.* **10**, 5032–5036 (2010)
19. Z. Ren, A. A. Taskin, S. Sasaki, K. Segawa, and Y. Ando, *Phys. Rev. B* **82**, 241306(R) (2010)
20. A. A. Taskin, Z. Ren, S. Sasaki, K. Segawa, and Y. Ando, *Phys. Rev. Lett.* **107**, 016801 (2011)
21. D. Kim, *et al*, *Nat. Phys.* **8**, 459–463 (2012)
22. H. Tang, D. Liang, L. J. Qiu, and P. A. X. Gao, *ACS Nano* **5**, 7510–7516 (2011)
23. M. Tian, *et al*, *Sci. Rep.* **3**, 1212 (2013)
24. M. T. Edmonds, *et al*, *ACS Nano* **8**, 6400–6406 (2014)
25. B. Sacepe, *et al*, *Nat. Commun.* **2**, 575 (2011)
26. D. A. Kozlov, *et al*, *Phys. Rev. Lett.* **112**, 196801 (2014)
27. Y. S. Fu, *et al*, *ACS Nano* **7**, 4105–4110 (2013)
28. B. Xia, *et al*, *Phys. Rev. B* **87**, 085442 (2013)
29. L. Bao, *et al*, *Sci. Rep.* **2**, 276 (2012)
30. R. Xu, *et al*, *Nature* **390**, 57–60 (1997)
31. A. Husmann, *et al*, *Nature* **417**, 421–424 (2002)
32. M. M. Parish, and P. B. Littlewood, *Nature* **426**, 162–165 (2003)
33. W. Zhang, *et al*, *Phys. Rev. Lett.* **106**, 156808 (2011)
34. A. Sulaev, *et al*, *AIP Adv.* **3**, 032123 (2013)
35. S.G. Lee, *et al*, *Nano Lett.* **12**, 4194–4199 (2012)
36. H. Fritzsche, *Phys. Rev.* **99**, 406 (1955)
37. M. Lang, *et al*, *ACS Nano* **6**, 295–302 (2011)
38. D. Shoenberg, *Cambridge University Press* (1984)
39. B. Hamdou, J. Gooth, A. Dorn, E. Pippel, and K. Nielsch, *Appl. Phys. Lett.* **103**, 193107 (2013)
40. P. Gehring, B. F. Gao, M. Burghard, and K. Kern, *Nano Lett.* **12**, 5137–5142 (2012)

41. R. W. Reinthaler, and E. M. Hankiewicz, *Phys. Rev. B* **85**, 165450 (2012)
42. M. Veldhorst, M. Sneider, M. Hoek, T. Gang, V. K. Guduru, X. L. Wang, U. Zeitler, W. G. van der Wiel, A. A. Golubov, H. Hilgenkamp, and A. Brinkman, *Nat. Mat.* **11**, 417 (2012)
43. F. X. Xiu, L. He, Y. Wang, L. Cheng, L. T. Chang, M. Lang, G. Huang, X. F. Kou, Y. Zhou, X. W. Jiang, Z. G. Chen, J. Zou, A. Shailos, and K. L. Wang, *Nat. Nano.* **6**, 216 (2011).

Chapter 5. Electrically tunable in-plane anisotropic magnetoresistance in nanoflake devices of topological insulator BiSbTeSe₂

For this project we have picked BiSbTeSe₂ as topological insulator material to study anisotropic magnetoresistance (AMR). We'll present the AMR measurements taken with different gate voltage, temperature, magnetic field, and current densities. Also theoretical model for the AMR phenomenon in the topological insulator materials will be given.

Theoretical work in this work is done by Prof. Shen Lei's group students Minggang Zeng and Yuan Ping Feng.

5.1. Introduction

The resistivity in materials may depend on the relative orientation of the current density $\vec{J}$ and applied magnetic field, which is usually named as anisotropic magnetoresistance (AMR). If both the current and the applied magnetic field are in the same plane of the sample, the resistivity variation is referred as an in-plane AMR. In-plane AMR is usually found in ferromagnetic materials, such as ferromagnetic metals,¹⁻³ magnetic semiconductors,⁴⁻⁵ and magnetoresistive oxides⁶⁻⁸. Assuming $\vec{J} = j_x \hat{x}$ and the magnetization (M), in the x - y plane, makes an angle $(\theta_{M,J})$ with $\vec{J}$. The induced electric field can be expressed as

$$E_x = \rho_{\perp} j_x + (\rho_{\parallel} - \rho_{\perp}) j_x \cos^2(\theta_{M,J}) \quad (5.1.1)$$

$$E_y = (\rho_{\parallel} - \rho_{\perp}) j_x \sin(\theta_{M,J}) \cos(\theta_{M,J}), \quad (5.1.2)$$

where $\rho_{//}$ and $\rho_{\perp}$ are the resistivity when $\theta_{M,J} = 0^\circ$ and 90° , respectively. The in-plane AMR value is usually defined as

$$AMR = \frac{\rho_{\perp} - \rho_{//}}{\rho_{\perp}}. \quad (5.1.3)$$

In ferromagnetic materials, the orientation of magnetization is determined by the direction and magnitude of the applied magnetic field and internal magnetic anisotropy of the material system. Experimentally, it is more convenient to measure the variation of resistivity along a direction that makes an angle ($\theta_{H,J}$) with the applied magnetic field. In ferromagnetic materials, the in-plane AMR is due to the spin-orbit interaction and spin-polarized electron transport. It is a very useful tool for studying the underlying physical mechanisms of electron transport.³⁻⁵ McGuire and Potter¹ predicted that the sign of AMR in a ferromagnetic material is determined by the spin polarization of transport electrons. If a spin polarized material has a positive in-plane AMR ($\rho_{//} < \rho_{\perp}$), it would show a negative in-plane AMR ($\rho_{//} > \rho_{\perp}$) if the spin polarization can be reversed. This theoretically predicted correlation between AMR and spin polarization has been experimentally confirmed in a ferromagnetic system with tunable spin-polarization, $\text{Co}_{1-x}\text{Fe}_x\text{S}_2$.⁹⁻¹⁰ Therefore, in-plane AMR can be used as a strong experimental evidence of the existence of spin-polarized current. In-plane AMR based applications in spintronics have also been proposed.⁵⁻⁸ As the in-plane AMR can generate a voltage along the y direction which can change from positive to negative (Eq. 5.1.2), it can be used for designing logic and magnetic random access memory devices,^{5,8} where the absolute value of $\rho_{\perp} - \rho_{//}$ determines the sensitivity of the devices. Furthermore, the first electric gate tuned in-plane AMR has been discovered in dilute magnetic semiconductor (Ga, Mn)As,⁴ which offers new possibilities for attaining great improvements in performance over metallic devices.

Topological insulator (TI) is a novel state of quantum matter characterized by Z_2 invariant. It is composed of fully filled insulating bulk states and metallic topological surface states (TSS).¹¹⁻¹³ The spin and momentum of Dirac electrons in TSS satisfy a helical lock-in relation, which has been confirmed experimentally by angle-resolved photoemission spectroscopy (ARPES).¹⁴⁻²¹ To date, extensive transport measurements on TI have been performed,²²⁻⁴¹ including preliminary measurements of in-plane magnetoresistance in Bi_2Se_3 and $(\text{Bi}, \text{Sb})_2\text{Se}_3$ thin films^{37,41} and in-plane AMR in TI/ferromagnet heterostructure⁴⁰. Several theoretical predictions have also been made about the effect of in-plane magnetic field and electric field on topological surface states⁴²⁻⁴⁴. However, due to the large bulk conductance contribution in prototype 3D TIs, such as Bi_2Se_3 and Bi_2Te_3 , electric gate tuned in-plane AMR of TI has never been reported. Recently, $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ has been confirmed to be a TI system.^{36,38,45,46} For certain x and y values, the material system can have large bulk resistivity and therefore significant surface transport can be realized. In our recent work, surface dominated transport and significant ambipolar behaviour have been realized in nanoflake devices of $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ ($x = 0.5$, $y = 0.4$)⁴⁶, which paves the way for further electron and spin transport study with applied gate voltage in TIs.

Here, we report the electric gate tuned in-plane AMR in *non-magnetic* nanoflake devices of TI BiSbTeSe_2 (BSTS). The in-plane AMR value of BSTS device is larger than that of transition metals, such as Fe, Ni, and Co. Moreover, we demonstrate, for the first time, continuous tuning of the in-plane AMR, from positive to negative, by an electric gate voltage. In order to understand the effects of gate electric field, current density, temperature and magnetic field on the in-plane AMR, we carry out first-principles calculations and propose a physical model, based on the in-plane magnetic field induced shift of the spin-momentum locked TSS. Due to the large resistivity of the device, the value of $\rho_{\perp} - \rho_{\parallel}$ is 4 orders magnitude larger than reported values in metallic ferromagnet, which provides the possibility

of fabricating more sensitive logic and magnetic random access memory AMR device once we can obtain TIs exhibiting the same properties at lower fields and room temperature.

5.2. Gate voltage dependence of BiSbTeSe₂ AMR

High quality BSTS single crystals were grown using a modified Bridgeman method in a furnace with a large temperature gradient. The sample growth has been described in details elsewhere.⁴⁶ Nanoflakes were obtained by mechanical exfoliation. Photolithography was used to pattern electrodes on the exfoliated nanoflakes. Cr/Au (5 nm/120 nm) contacts were deposited in a magnetron sputtering system with a base pressure of 1×10^{-8} torr. The magnetotransport measurements were performed in a Physical Property Measurement System (PPMS, Quantum Design). All measurements in this work were carried out employing a DC current.

Figure 5.2.1. The gate dependence of resistance (R_{xx}) in the absence of external magnetic field and Hall resistance (R_{xy}) at 1 Tesla field of a BSTS nanoflakes device at 2 K. The inset shows an image of the device fabricated using standard photolithography.

Figure 5.2.2. (a) The image of device 1. (b) A schematic diagram of the AMR measurement setup. (c) and (d) show the gate voltage dependence of the ambipolar effect (the purple circles) and AMR amplitude of device 1 at 2 K under 1 T and 9 T magnetic field, respectively. (e) The in-plane AMR of device 1 under 1 T magnetic field at 2 K with $V_g = +50$ V, +30 V, 0 V, -10 V, -30 V, and -50 V gating voltage, respectively. (f) The in-plane AMR of device 1 under 9 T magnetic field at 2 K with $V_g = +50$ V, +30 V, 0 V, -10 V, -30 V, and -50 V gating voltage, respectively.

As mentioned above, surface dominated transport can be realized in the BSTS nanoflake devices with thickness of several hundred nanometers. Due to the surface dominated transport, we are able to observe pronounced ambipolar electric effect in devices with thickness of 100 ~ 300 nm. Figure 5.2.1 shows the typical gate voltage (V_g) dependence of longitudinal resistance (R_{xx}) in the absence of external magnetic field, and Hall resistance (R_{xy}) at a magnetic field of 1 Tesla. The image of the device is shown in the inset in Fig. 5.2.1. The Hall resistance was measured at both 1 T and -1 T and then calculated using $[R_{xy}(1\text{ T}) - R_{xy}(-1\text{ T})]/2$ to eliminate possible non-symmetry effect of the sample and electrode contact induced magnetoresistance. The maximum in resistance (the charge neutrality point) appears near $V_g = -8\text{ V}$. The resistance changes by nearly 70% within the range of -50V to + 50 V. The gradual decrease of resistance with V_g beyond the charge neutrality point indicates that the ambipolar behaviour is caused by the Dirac cone of the topological surface state. The transition from *n*-type to *p*-type is shown in the gate voltage dependence of Hall resistance.

Electric gate tuned in-plane AMR under various gate electric field, current density, temperature and magnetic field was measured in more than 10 standard four-contact devices. The image of a typical device and schematic experimental set-up are shown in Figs. 5.2.2(a) and 5.2.2(b), respectively, where θ is the angle between the magnetic field and the direction perpendicular to the current. When $\theta = 0^\circ$, the magnetic field is perpendicular to the current. When $\theta = 90^\circ$, the magnetic field is parallel to the current. In this paper, we present the results of the in-plane AMR of three devices, device 1, device 2 and device 3. The ambipolar effect is observed in device 1 and device 2, which means that the dominated surface transport is realized in the two devices. For comparison, we also deliberately chose device 3, which does not exhibit a clear ambipolar effect. It should be emphasized that other devices showing pronounced ambipolar effect manifest the same characteristics as devices 1 and 2 in the in-

plane AMR measurements, while the devices without a clear ambipolar effect exhibit the same properties as device 3.

As shown by the red dotted curves in Figs. 5.2.2(c) and 5.2.2(d), similar to many other devices fabricated by BSTS, device 1 which is 187 nm thick shows a pronounced Dirac-type ambipolar curve with a resistance maximum at -2 V, which illustrates that we can easily tune the Fermi level and electron transport. A pronounced gate-tuned in-plane AMR effect is observed in the four-contact device (Fig. 5.2.2(a)). The results of the in-plane AMR measurements for device 1 at 1 T and 9 T under various gate voltage are shown in Figs. 5.2.2(e) and 5.2.2 (f), respectively. The AMR amplitudes are calculated using

$$AMR\ amplitude = \frac{\rho_{\max} - \rho_{\min}}{\rho_{\min}}, \quad (5.2.1)$$

where $\rho_{\max}$ and $\rho_{\min}$ are the maximum and minimum values of the resistivity, respectively. From the in-plane AMR at 9 T field (Fig. 5.2.2 (f)), we can easily identify three special characteristics. Firstly, similar to the in-plane AMR effect in transition metals, the AMR exhibits an oscillatory behavior with a period of 180° . However, the shape of the AMR curve cannot be described as a cosine curve as shown in Eq. 5.1.1, which is only suitable for materials without crystalline anisotropy. Secondly, the AMR evolves gradually from positive ($\rho_{//} < \rho_{\perp}$) to negative ($\rho_{//} > \rho_{\perp}$) when the V_g varies from +50 V to -50 V, which has never been reported in any systems prior to our work. As shown in Fig. 5.2.2 (f), at $V_g = +50$ V, a positive AMR is observed, while a negative AMR is observed at $V_g = -50$ V. The in-plane AMR at $V_g = 30$ V, 0 V, -10 V and -30 V clearly display that the in-plane AMR peaks shift gradually in the process of V_g variation from +50 V to -50 V. Thirdly, the largest AMR amplitude is shown near the charge neutrality point. As shown in Figs 5.2.2(f) and 5.2.2(d), the voltage dependence of the AMR shows a peak value 9% at $V_g = +10$ V, which is even

larger than the AMR amplitude of transition metals with strong ferromagnetism, such as Fe, Ni, etc, although BSTS is a non-ferromagnetic material. When the gate voltage deviates from the charge neutrality point, the amplitude of AMR decreases. The ratio of the peak value (at $V_g = +10$ V) to the minimum value (at $V_g = -30$ V) is 2.5. The measurement results under 1 T magnetic field are plotted in Figs. 5.2.2(e) and 5.2.2(f), which also show a period of 180° , a change of the sign, and a tunable magnitude of AMR value. However, the change of sign happens at more negative gate voltage and the minima of the AMR value appears at -50 V. It should be noticed that the resistivity of the BSTS device is $\sim 0.1 \Omega\cdot\text{cm}$. The absolute value of $\rho_\perp - \rho_\parallel$ is 4 orders larger than previously measured values in metallic ferromagnet and therefore the electric field obtained along y direction, as shown in Eq. 5.1.2, will be 4 orders larger. This indicates that topological insulators may be a promising material system for in-plane AMR based logic and magnetic random access memory devices if we can realize the effect in higher temperature and lower magnetic field.

Figure 5.2.3. (a) The in-plane AMR of the fresh device 2 under 1 T magnetic field at 2 K with $V_g = +50\text{ V}$, $+25\text{ V}$, 0 V , -25 V , and -50 V , respectively. (c) The in-plane AMR of the aged device 2 under 1 T magnetic field at 2 K with $V_g = +50\text{ V}$ and -47 V , respectively. (e) The in-plane AMR of device 3 under 1 T magnetic field at 2 K with $V_g = +25\text{ V}$, 0 V , -25 V and -50 V , respectively. (b), (d) and (f) show the gate voltage dependence of the ambipolar effect (the blue circles) and the amplitude of AMR value (the red dots) at 2 K of the fresh device 2, aged device 2 and device 3, respectively.

To investigate the origin of the large in-plane AMR, two comparison experiments were performed. The first experiment shows the aging effect. We measured the in-plane AMR of another device with pronounced ambipolar effect (device 2) and then placed it in a dry box for 10 days. Thereafter, we measured the ambipolar effect and in-plane AMR again. As shown in Figs. 5.2.3(a) and 5.2.3(b), the fresh device 2 shows large AMR amplitudes (2.5 - 4 %) from $V_g = 0$ V to 50 V. The AMR amplitude decreases fast at the negative V_g side. It gets to ~ 1 % at -50 V. The comparison between the electric field ambipolar curve and AMR value under various voltage in Fig. 5.2.3(b) clearly shows characteristics similar to that of device 1 (Figs. 5.1.2(c) and 5.1.2(d)). The electric field ambipolar effect and in-plane AMR show dramatic change after the storage of ten days in dry air. Figs. 5.2.3(c) and 5.2.3(d) illustrate the shift of the charge neutrality point of the ambipolar curve and the decrease of the in-plane AMR. The highest AMR amplitude of the fresh device 2 (3.68%) shows at $V_g = 25$ V, which is 27 V higher than the voltage at the charge neutrality point. In the aged device 2, the point of 27 V higher than the neutrality point is -47 V, where the AMR amplitude has a much lower value (2%). This observation of the aging experiment suggests a strong correlation between the electric ambipolar effect and in-plane AMR, which indicates a surface origin of the in-plane AMR. In the second comparison experiments, we deliberately chose devices showing unclear ambipolar behaviour to perform the AMR measurements. The results of one of the devices (device 3) are shown in Figs. 5.2.3(e) and 5.2.3(f). It is very clear that the device shows small in-plane AMR at all applied gate voltage. Because the unclear ambipolar behaviour means large bulk conductance contribution, this experiment further strongly supports that the large AMR effect in device 1 and 2 is contributed by surface states.

Figure 5.2.4. (a) The in-plane AMR of device 1 under 1 T magnetic field and $V_g = +10\text{ V}$ at 2 K with different current densities. (b) The variation of AMR amplitude with increasing current density at 2 K for three different measurement conditions, (1) $B = 1\text{ T}$ and $V_g = +10\text{ V}$, (2) $B = 1\text{ T}$ and $V_g = -50\text{ V}$, and (3) $B = 9\text{ T}$ and $V_g = -50\text{ V}$.

Figure 5.2.5. (a) The in-plane AMR of device 1 under 9 T magnetic field and $V_g = +10$ V at different temperatures. (b) The in-plane AMR of device 1 under 9 T magnetic field and $V_g = -50$ V at different temperatures. (c) and (d) show the schematic diagram of the excitation of electrons by thermal energy, when the Fermi level is located above and below the Dirac point, respectively. (e) and (f) show the temperature dependence of the ambipolar effect and AMR amplitude under 9 T magnetic field with $V_g = +10$ V and -50 V, respectively.

To further investigate the in-plane AMR in BSTS devices, we performed measurements on device 1 under various current densities, magnetic fields and temperatures. In order to investigate the effect of current density, we performed three sets of experiments, (1) $B = 1$ T and $V_g = +10$ V, (2) $B = 1$ T and $V_g = -50$ V, (3) $B = 9$ T and $V_g = -50$ V, at $T = 2$ K with current density varying from 25 nA to 500 nA. Figure 5.2.4(a) shows the in-plane AMR curves under various current densities at $V_g = 10$ V and $B = 1$ T. Figure 5.2.4(b) depicts the amplitude of AMR under various current densities for the three conditions as aforementioned. The measurement results verify that the variation of current density does not change the shape and value of the AMR. The temperature dependence of the in-plane AMR of device under 9 T field at $V_g = 10$ V and -50 V is shown in Fig. 5.2.5. At 2 K, the AMR at $V_g = 10$ V shows the minima when the magnetic field is parallel to current (Fig. 5.2.5(a)), while the AMR at -50 V has a 90° phase shift and shows the minima when magnetic field is perpendicular to the current (Fig 5.2.5(b)). With the temperature dependent measurement, the AMRs at $V_g = 10$ V and -50 V show totally different behaviour. It is observed that the peaks of the in-plane AMR shift with increasing temperature in both cases. Remarkably, at 70 K and 80 K, we observe very similar AMR curves at the two applied V_g as shown in Figs. 5.2.5(a) and 5.2.5(b). The comparisons between the electric field ambipolar effect and the decay of the amplitude of AMR at $V_g +10$ V and -50 V are plotted in Figs. 5.2.5(c) and 5.2.5(d), respectively. The amplitude of the AMR decreases ~ 6 times with the increase of temperature from 2 K to 80 K, while the electric field ambipolar effect only decreases ~ 2 times. The magnetic field dependences of the in-plane AMR of device 1 at $V_g = +10$ V and -50 V are shown in Figs. 5.2.6(a) and 5.2.6(b), respectively. It is clearly evident that the sign of AMR does not change with increasing magnetic field. The $\rho_\perp$ is always larger than $\rho_\parallel$ at $V_g = +10$ V, while $\rho_\perp$ remains smaller than $\rho_\parallel$ at $V_g = -50$ V. Figures 5.2.6(c), 5.2.6(d) and

5.2.6(e) show the magnetic field dependence of the AMR amplitude of device 1 at $V_g = +10$ V, $V_g = -50$ V, and device 2 at $V_g = +25$ V respectively.

Figure 5.2.6. (a) and (b) show the in-plane AMR of device 1 at 2 K under various magnetic fields with $V_g = +10$ V and -50 V, respectively. (c), (d) and (e) show the magnetic field dependence of AMR amplitude at 2 K with $V_g = +10$ V, -50 V, and $+25$ V, respectively.

5.3. Theoretical model

Works on theoretical model were led by Professors Shen Lei and Han Yuan Ping from Department of Physics, National University of Singapore, and Sergey Eremeev from Tomsk State University.

We need to consider various physical reasons which can be responsible for the origin of the in-plane AMR, such as the anisotropy of crystal structure, orbital motion of carriers, weak anti-localization, Zeeman splitting, gap opening at the Dirac point, and spin-momentum locking induced spin-polarized topological surface transport etc. BSTS has a Bi_2Te_3 -like hexagonal crystal structure, so that crystal anisotropy can be easily dismissed as the origin for our in-plane AMR effect that has a period of 180° . Experimental results from another group had also demonstrated that the in-plane MR transition of hexagonal TI Bi_2Se_3 is irrelevant to the crystal anisotropy.⁴¹ For a non-magnetic quasi-2D electron gas, the in-plane AMR can originate from the orbital motion of carriers.^{48,49} However, the origin of the orbital motion cannot explain the evolution of the AMR from positive to negative with applied V_g , i.e., hole/electron behavior by tuning the chemical potential. Weak localization and Weak anti-localization have been proposed as one of the origin of in-plane magnetoresistance³⁷ in topological insulator and other materials.⁴⁹ At the same time, the WAL or WL can be suppressed or smeared out by thicker samples.²⁹ Our experiment shows that the AMR of 100 - 300 nm thick devices increases with increasing field up to 9 T. Moreover, weak anti-localization cannot induce the sign change of AMR via a gate voltage. Thus, these experimental evidences indicate that WAL is not the origin of the AMR effect. The same conclusion is also obtained by the MR measurement of Bi_2Se_3 under parallel magnetic field.⁴¹ We also can exclude the Zeeman-split term induced by a 9 T magnetic field. It is because there is a strong SOC in TIs, which can diminish and even entirely suppress the Zeeman-split term.⁵⁰ Moreover, gap opening at the Dirac point can clearly be ruled out because the in-

plane magnetic field cannot induce perpendicular magnetism of topological surface state, and thus cannot open the gap in the Dirac point.^{51,52}

Figure 5.3.1. The optimized structures of the BiSbTeSe₂ unitcell (a) and 8QL BiSbTeSe₂ slab (b).

As aforementioned, the in-plane AMR with a period of 180° is a standard behavior of spin-polarized electronic transport. Hence, the natural origin for the electric tuned AMR in TI probably is spin-related. Detailed analysis of the correlation between the electric gate dependence of the ambipolar effect and the in-plane AMR can elucidate the origin of the in-plane AMR. As shown in Figs. 5.2.2(c), 5.2.2(d) and 5.2.3(b), the charge neutrality points of both device 1 and device 2 are around 0 V, which means that the Fermi level lies in close vicinity to the Dirac point of the topological surface state and in the band gap of the bulk state. It should also be noticed that the largest values of in-plane AMR are also near the charge neutrality points. They are around $V_g = +10$ V and $+25$ V for device 1 and device 2, respectively. It is therefore clearly evident that the Fermi level is in the band gap when the largest AMR value is obtained. Furthermore, deviating from the AMR maxima, the amplitude of the in-plane AMR decreases when the gate voltage varies to both large negative and positive values, which means that the in-plane AMR decreases when Fermi level approaches the bulk band. Thus, we conclude that the in-plane AMR should originate from the topological surface state.

As pointed above, the spin-polarized electron transport and spin-orbit interaction induce the in-plane AMR effect in ferromagnetic materials. Both the theory and experiment^{1,9,10} have demonstrated that the AMR value can evolve from positive to negative when the spin polarization of transport carriers changes signs. For topological insulators, it is still valid. It is well known that the in-plane magnetic field produces a relative shift of the in-plane momentum (decoupling of the surface states).^{42, 53, 54} Based on this understanding, we carry out first-principle calculations and build a physical model in the following. The topological surface state and its spin texture in a BSTS slab are calculated by first-principles calculations. In our model the relative shift of the Fermi contours of the top and bottom surface states

caused by the in-plane magnetic field generates a net spin-polarization, of which the orientation is dependent on the direction of the magnetic field.

Figure 5.3.2. (a) The calculated band structure of the BiSbTeSe₂ slab (violet line). The bulk bands are projected onto the two-dimensional Brillouin zone (filled blue area). (b) and (c) are the calculated Fermi contours for top- and bottom-side surface states with the energy sampling at the black solid-line in (a).

Our first-principles calculations were carried out using the VASP⁵⁵. The generalized gradient approximation of Perdew, Burke, and Ernzerhof to the exchange-correlation potential has been used. The interaction between the ion cores and valence electrons was described by the projector augmented-wave method⁵⁶. The spin-orbit interaction (SOI) was included in the calculations. To simulate BSTS compound within supercell approach we have chosen ordered BiSbTeSe₂ system, which is only slightly Se-enriched compared with the experimental composition. To preserve inversion symmetry in the system the unit cell is doubled in direction of hexagonal axis as compared to the parent Bi₂Se₃ cell. The optimized bulk rhombohedral unit cell is shown in Fig. 5.3.1(a). The slab calculation is based on a 8 quintuple layers (QLs) of BiSbTeSe₂ (Fig.5.3.1(b)). All the bulk and slab structures were

relaxed until the force on each atom is smaller than 0.01 eV/Å. The cutoff energy was taken to be 400 eV and k -point meshes of $5 \times 5 \times 5$ and $8 \times 8 \times 1$ were used for the bulk and slab calculations, respectively.

The calculated band structure of the slab (Fig. 5.3.2 (a)) shows the doubly degenerate topological surface states with a single Dirac cone at $\bar{\Gamma}$ resided in the bulk energy gap of 0.21 eV, which is similar to the calculated band structure of the Bi_2Se_3 slab.⁵⁷ Figures. 5.3.2(b) and 5.3.2(c) show the calculated spin texture of the surface states with the energy level sampling near the Dirac point. The spin texture shows spin-momentum-locked pattern and has opposite spin helicities on the top and bottom surfaces.

Figure 5.3.3. (a) Schematic of two surface states in a 3D topological insulator. The red and blue curves represent the edge current with opposite spin character. (b) The in-plane magnetic field induced Dirac cone shift of the top and bottom topological surface states. (c) and (d) Schematic diagram of the in-plane magnetic field induced Fermi circle shift and net spin. (e) The relationship between the value of the net spin polarization and the magnitude of magnetic field.

The schematic picture of two surface states in a 3D TI nanoflake is shown in Fig. 5.3.3(a). The red and blue curves represent the current with opposite spin helicities. Note that under a bias voltage (the x direction), the top and bottom surface Dirac electrons are coupled or mixed driven by bias voltage in transport experiment (*dynamic*) as shown in Fig. 5.3.3(a) because all surfaces are transport channels and contribute to the transport in the device, while the two surface electrons are not coupled in a thick sample without bias voltage (*static*). For example the calculations show that 6QLs thickness of Bi_2Se_3 can decouple the top and bottom surface states.^{13,14,42,58} If an in-plane magnetic field is applied on the surface of TIs, for example, $B = B_y \hat{y}$, it can lead to the relative momentum shift $p_x = q$ between the top and bottom surface states as shown in Fig. 5.3.3(b), where $q = eB_y d\hat{x}$. Such opposite in-plane momentum shift likes the Rashba splitting with the Rashba coefficient of $q/2$. From Figs. 5.3.3(c) and 5.3.3(d), we can see a momentum shift of the two topological surface states, which is induced by the in-plane magnetic field, can generate a *net* spin polarization. The orientation of the net spin polarization is parallel to the applied magnetic field and hence rotates with the magnetic field relative to the current in our experiment. Moreover, the net spin polarization is proportional to the magnetic field as illustrated in Fig. 5.3.3(e). For example, the estimation of the net spin polarization (S_{net}) on the base of calculated in-plane spin components S_{xy} for the BSTS slab and magnetic fields of 1T and 9T gives the values of 0.04 and 0.36, respectively. The theory of McGuire and Potter indicates that in-plane AMR is induced by the spin polarization rotating with applied magnetic field, which generates the different scattering probability for different angles between the current and applied magnetic field.¹ This explains the observed in-plane AMR with a period of 180° in our experiment (Figs. 5.2.2 – 5.2.6).

Figure 5.3.4. Schematic diagram of the top and bottom topological surface states with an in-plane magnetic field under different gate voltages. (a) The Fermi level is higher the Dirac point. The carriers are n-type Dirac electrons; (b) the Fermi level is lower than the Dirac point. The carriers are p-type Dirac holes. It shows that the same direction of applied magnetic field can generate different direction of net spin polarization because of the different helical spin characters of Dirac electrons and holes.

Figure 5.3.4 shows the schematic diagram of two topological surface states under different gate voltages. The chemical potential of two Dirac cones is shifted by the gate voltage.²⁹ Because of the opposite spin helicities of Dirac electrons and holes in the topological surface states, the net spin, S_{net} , with opposite orientation is generated [lower panel of Figs. 5.3.4(a) and 5.3.4(b)]. Here, the direction of magnetic field is along x . According to the McGuire and Potter's theory¹ and experiments on a tunable highly spin polarized system^{9,10}, the sign of the in-plane AMR is determined by the sign of the spin polarization. The opposite net spin polarization of Dirac carriers (electrons and holes) is the reason of the opposite sign of AMR in the experiment under $+50\text{V}$ and -50V gate voltages (Figs. 5.2.2(e) and 5.2.2(f)). At $V_g = +50\text{V}$, both of the top and bottom surfaces are n-type.

The net spin polarization is positive and therefore generate the positive AMR in the TI system. At $V_g = -50$ V, both of the top and bottom surfaces are p-type. As shown in Fig. 5.3.4(b), the in-plane magnetic field induces negative net spin polarization. Therefore, the p-type helical carriers show negative AMR. The AMR curves show gradual change from positive to negative when the V_g varies from +50 V to -50 V.

The scenario can also explain the evolution of in-plane AMR with various current densities, magnetic fields and temperatures as shown in Figs. 5.2.4, 5.2.5 and 5.2.6, respectively. The measurement results as shown in Fig. 5.2.4 verify that the variation of current density does not change the shape and value of the AMR, which agrees with the above theoretical analysis.

Figure 5.3.5. Schematic diagrams of the electron thermal excitation in Dirac cones under different gate voltage (a) negative -50 V and the Fermi level is below the Dirac point, (b) positive 10 V and the Fermi level is above the Dirac point.

The temperature dependence of in-plane AMR can be clarified by the thermal energy induced carrier excitation. At 2 K, as shown in Fig. 5.3.4, the spin polarization of carriers at $V_g = +10$ V (electron) and -50 V (hole) has opposite sign, and therefore induces a positive and negative AMR, respectively. With the increase of temperature, some electrons can be excited to higher energy levels. To clarify our idea, the schematic diagrams of the electron excitation

in Dirac cones are plotted in Fig. 5.3.5. From the diagram, we can easily see the difference between $V_g = -50$ V and $+10$ V. At $V_g = -50$ V, the Fermi level is located below the Dirac point (called "hole phase" in Fig. 5.3.5(a)). There are continuous available states from the Fermi level to high energy levels. Hence, even small thermal agitation energy can excite electrons to the energy levels above the Dirac point (called "electron phase" in Fig. 5.3.5(d)) by multiple excitations. With further increase in temperature, the transport contributed by the electrons above the Dirac point becomes more and more important. The gradual evolution of AMR ("phase transition") with increasing temperature is clearly reflected in Fig. 5.3.5(a). The temperature evolution of AMR at $V_g = +10$ V is very different from that at $V_g = -50$ V. As shown in Fig. 5.3.5(b), at $V_g = +10$ V, the Fermi level is located above the Dirac point, i.e., electron phase is realized. After electron excitation at high temperature, it is always "electron phase", i.e., no phase transition occurs. From Figures. 5.3.5(a) and 5.3.5(b), one can expect that the AMR curves at $V_g = +10$ V and -50 V should be similar at high temperature, which has been proved in Fig. 5(a) and 5(b). This indicates that the distribution of electrons around the Dirac point for $V_g = +10$ V and -50 V are similar at high temperature (70-80 K) because of the thermal excitation. Furthermore, the amplitude of the AMR decreases by ~ 6 times with the increase of temperature from 2 K to 80 K (Fig. 5.2.5(b) and (c)). It is because of the co-existence of holes and electrons after electron excitation around the Dirac point [Figs. 5.3.5(a) and 5.3.5(b)]. In fact, the evolution of Aharonov-Bohm oscillations and Altshuler-Aronov-Spivak oscillations with temperature in TI nanowires may also lead to the same effect.^{59,60}

The experimental results in Fig. 5.2.6 show that the sign of AMR does not change with increasing magnetic field. This is a natural result based on our model, because the position of Fermi level in TI determines the spin polarization and the value of spin polarization determines the in-plane AMR. The magnitude of magnetic fields only determines the value of net spin (Fig. 5.3.3(e)) and then the amplitude of the AMR. Another interesting

observation is that the shape of the AMR curve evolves with increasing magnetic field, which is especially pronounced for the AMR at $V_g = -50$ V. In ferromagnetic materials, the shape of AMR is determined by the existence of various anisotropic energies. The spins do not rotate smoothly with the rotating magnetic field due to the competition between the anisotropic energy and the Zeeman energy of the spin and magnetic field. The manifestation of different shape under different magnetic field in our experiments probably also indicates anisotropy. The amplitude of the normal in-plane AMR effect in ferromagnetic materials usually saturates at the field where the magnetic moment is saturated (a full alignment of the spins with the magnetic field). The field dependence of in-plane AMR of different BSTS devices show different behaviour. As mentioned previously, the variation of the AMR amplitude with magnetic field for device 1 at $V_g = +10$ V, -50 V, and device 2 at $V_g = +25$ V are plotted in Figs. 5.2.6(c), (d) and (e), respectively. As shown in Fig. 5.2.6(e), the in-plane AMR in the device 2 increases with increasing field from 1 to 4 T and then shows saturation behaviour from 4 T to 9 T. For device 1 the in-plane AMR increases with increasing magnetic field up to 9 T. As shown in Fig. 5.3.3(e), the net spin polarization increases with increasing magnetic field and therefore induces increasing in-plane AMR. The saturation behaviour shown in device 2 may be due to the small size of Fermi circles .

5.4. Conclusion

In conclusion, we have observed a large electrically tunable in-plane AMR effect in nanoflake devices of non-magnetic TI BSTS. For the first time, a large in-plane AMR, which can be tuned from negative to positive by electric gate voltage, is realized. The effects of gate electric field, current density, temperature and magnetic field on the in-plane AMR are explained by a physical model and first-principles calculations. The absolute value of the

anisotropic resistivity ($\rho_{\perp} - \rho_{\parallel}$) is 4 orders magnitude larger than previously observed values in metallic ferromagnet, which makes topological insulator to be a promising material system for fabricating in-plane AMR based logic and magnetic random access memory devices if the effect can be realized at higher temperatures and lower magnetic fields in future.

Reference

1. T.R. McGuire and R.I. Potter, *IEEE Trans. Magn.* **11**, 1018 (1975)
2. D.A. Thompson, L.T. Romankiw, and A.F. Mayadas, *IEEE Trans. Magn.* **11**, 1039 (1975)
3. G.H. Li, T. Yang, Q. Hu, H.G. Jiang, and W.Y. Lai, *Phys. Rev. B* **65**, 134421 (2002)
4. D. Chiba, M. Sawicki, Y. Nishitani, Y. Nakatani, F. Matsukura, and H. Ohno, *Nature* **455**, 515 (2008)
5. H.X. Tang, K.K. Kawakami, D.D. Awschalon, and M.L. Roukes, *Phys. Rev. Lett.* **90**, 107201 (2003)
6. Y. Bason, L. Klein, J.B. Yau, X. Hong, and C.H. Ahn, *Appl. Phys. Lett.* **84**, 2593 (2004)
7. S.T.B. Goennenwen, R.S. Keizer, S.W. Schnick, I. Van Dijk, T.M. Klapwijk, G.X. Miao, G. Xiao, and A. Gupta, *Appl. Phys. Lett.* **90**, 142509 (2007)
8. Y. Bason, L. Klein, J. B. Yau, X. Hong, J. Hoffman, and C. H. Ann, *J. Appl. Phys.* **99**, 08R701 (2006)
9. L. Wang, K. Umemoto, R. M. Wentzcovitch, T. Y. Chen, C. L. Chien, J. G. Checkelsky, J. C. Eckert, E. D. Dahlberg, C. Leighton, *Phys. Rev. Lett.* **94**, 056602 (2005)
10. L. Wang, T. Y. Chen, C. L. Chien, J. G. Checkelsky, J. C. Eckert, E. D. Dahlberg, K. Umemoto, R. M. Wentzcovitch, C. Leighton, *Phys. Rev. B* **73**, 144402 (2006)
11. L. Fu, C. L. Kane, and E. J. Mele, *Phys. Rev. Lett.* **98**, 106803 (2007).
12. J. E. Moore, *Nature* **464**, 194 (2010).
13. X. L. Qi and S. C. Zhang, *Phys. Today* **63**, 33 (2010).
14. M. Z. Hasan and C. L. Kane, *Rev. Mod. Phys.* **82**, 3045 (2010).
15. P. D. C. King, R. C. Hatch, M. Bianchi, R. Ovsyannikov, C. Lupulescu, G. Landolt, B. Slomski, J. H. Dil, D. Guan, J. L. Mi, E. D. L. Rienks, J. Fink, A. Lindblad, S. Svensson, S. Bao, G. Balakrishnan, B. B. Iversen, J. Osterwalder, W. Eberhardt, F. Baumberger, and P. Hofmann, *Phys. Rev. Lett.* **107**, 096802 (2011)
16. L. Chen, J. G. Analytis, J. H. Chu, Z. K. Liu, S. K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z. X. Shen, *Science* **325**, 178 (2009).
17. D. Hsieh, Y. Xia, L. Wray, D. Qian, A. Pal, J. H. Dil, J. Osterwalder, F. Meier, G. Bihlmayer, C. L. Kane, Y. S. Hor, R. J. Cava, and M. Z. Hasan, *Science* **323**, 919 (2009).
18. T. Hirahara, Y. Sakamoto, Y. Takeichi, H. Miyazaki, S. I. Kimura, I. Matsuda, A. Kakizaki, and S. Hasegawa, *Phys. Rev. B* **82**, 155309 (2010).
19. C. Jozwiak, Y. L. Chen, A. V. Fedorov, J. G. Analytis, C. R. Rotundu, A. K. Schmid, J. D. Denlinger, Y. D. Chuang, D. H. Lee, I. R. Fisher, R. J. Birgeneau, Z. X. Shen, Z. Hussain, and A. Lanzara, *Phys. Rev. B* **84**, 165113 (2011).
20. K. Miyamoto, A. Kimura, T. Okuda, H. Miyahara, K. Kuroda, H. Namatame, M. Taniguchi, S. V. Ereemeev, T. V. Menshchikova, E. V. Chulkov, K. A. Kokh, O. E. Tereshchenko, *Phys. Rev. Lett.* **109**, 166802 (2012).
21. S. Souma, K. Kosaka, T. Sato, M. Komatsu, A. Takayama, T. Takahashi, M. Kriener, K. Segawa, and Y. Ando, *Phys. Rev. Lett.* **106**, 216803 (2011).
22. J. G. Analytis, J. H. Chu, Y. Chen, F. Corredor, R. D. McDonald, Z. X. Shen, and I. R. Fisher, *Phys. Rev. B* **81**, 205407 (2010).
23. Y. S. Hor, A. Richardella, P. Roushan, Y. Xia, J. G. Checkelsky, A. Yazdani, M. Z. Hasan, N. P. Ong, and R. J. Cava, *Phys. Rev. B* **79**, 195208 (2009).
24. J. G. Checkelsky, Y. S. Hor, R. J. Cava, and N. P. Ong, *Phys. Rev. Lett.* **106**, 196801 (2011).
25. D. Kim, S. Cho, N. P. Butch, P. Syers, K. Kirshenbaum, S. Adam, J. Paglione and M. S. Fuhrer, *Nat. Phys.* **8**, 459 (2012).

26. N. P. Butch, K. Kirshenbaum, P. Syers, A. B. Sushkov, G. S. Jenkins, H. D. Drew, and J. Paglione, *Phys. Rev. B* **81**, 241301 (2010).
27. D. X. Qu, Y. S. Hor, J. Xiong, R. J. Cava, and N. P. Ong, *Science* **329**, 821 (2010).
28. H. Peng, K. Lai, D. Kong, S. Meister, Y. Chen, X.-L. Qi, S.-C. Zhang, Z.-X. Shen, and Y. Cui, *Nat. Mater.* **9**, 225 (2010).
29. J. Chen, H. J. Qin, F. Yang, J. Liu, T. Guan, F. M. Qu, G. H. Zhang, J. R. Shi, X. C. Xie, C. L. Yang, K. H. Wu, Y. Q. Li, and L. Lu, *Phys. Rev. Lett.* **10**, 176602 (2010).
30. Y. S. Kim, M. Brahlek, N. Bansal, E. Edrey, G. A. Kapilevich, K. Iida, M. Tanimura, Y. Horibe, S. W. Cheong, and S. Oh, *Phys. Rev. B* **84**, 073109 (2011)
31. M. Liu, J. Zhang, C. Z. Chang, Z. Zhang, X. Feng, K. Li, K. He, L. L. Wang, X. Chen, X. Dai, Z. Fang, Q. K. Xue, X. Ma, and Y. Wang, *Phys. Rev. Lett.* **108**, 036805 (2012).
32. H. L. Cao, J. F. Tian, I. Miokowsky, T. Shen, J. N. Hu, S. Qiao, and Y. P. Chen, *Phys. Rev. Lett.* **108**, 216803 (2012)
33. H. T. He, G. Wang, T. Zhang, I. K. Sou, G. K. L. Wong, J. N. Wang, H. Z. Lu, S. Q. Shen, and F. C. Zhang, *Phys. Rev. Lett.* **106**, 166805 (2011).
34. S. Matsuo, T. Koyama, K. Shimamura, T. Arakawa, Y. Nishihara, D. Chiba, K. Kobayashi, T. Ono, C. Z. Chang, K. He, X. C. Ma, and Q. K. Xue, *Phys. Rev. B* **85**, 075440 (2012).
35. H. Steinberg, D. R. Gardner, Y. S. Lee and P. Jarillo-Herrero, *Nano Lett.* **10**, 5032 (2010).
36. Z. Ren, A. A. Taskin, S. Sasaki, K. Segawa, and Y. Ando, *Phys. Rev. B* **82**, 241306 (2010).
37. C. J. Lin, X. Y. He, J. Liao, X. X. Wang, V. Sacksteder, W. M. Yang, T. Guan, Q. M. Zhang, L. Gu, G. Y. Zhang, C. G. Zeng, X. Dai, K. H. Wu, Y. Q. Li, *Phys. Rev. B* **88**, 041307 (2013)
38. A. A. Taskin, Z. Ren, S. Sasaki, K. Segawa, and Y. Ando, *Phys. Rev. Lett.* **107**, 016801 (2011)
39. S. S. Hong, J. J. Chua, D. S. Kong, and Y. Cui, *Nat. Comm.* **3**, 757 (2012)
40. B. Xia, P. Ren, A. Sulaev, Z. P. Li, P. Liu, Z. L. Dong, and L. Wang, *AIP advances* **2**, 042171 (2012)
41. J. Wang, H. D. Li, C. Z. Chang, K. He, J. S. Lee, H. Z. Lu, Y. Sun, X. C. Ma, N. Samarth, S. Q. Shen, Q. K. Xue, M. H. Xie, M. H. W. Chan, *Nano Research* **5**, 739 (2012)
42. S. S. Pershoguba, V. Yakovenko, *Phys. Rev. B* **86**, 165402 (2012)
43. A. A. Zyuzin, M. D. Hook, and A. A. Burkov, *Phys. Rev. B* **83**, 245428 (2011)
44. Oleg V. Yazyev, J. E. Moore, and S. G. Louie, *Phys. Rev. Lett.* **105**, 266806 (2010)
45. T. Arakane, T. Sato, S. Souma, K. Kosaka, K. Nakayama, M. Komatsu, T. Takahashi, Z. Ren, K. Segawa, and Y. Ando, *Nat. Comm.* **3**, 636 (2012).
46. B. Xia, P. Ren, A. Sulaev, P. Liu, S. Q. Shen, and L. Wang, *Phys. Rev. B* **87**, 085442 (2013)
47. H. Z. Lu, and S. Q. Shen, *Phys. Rev. B* **84**, 125138 (2011).
48. S. Das Sarma and E. H. Hwang, *Phys. Rev. Lett.* **84**, 5596 (2000)
49. M. B. Lundeberg and J. A. Folk, *Phys. Rev. Lett.* **105**, 146804 (2010)
50. M. Hermanns, N. Regnault, B. A. Bernevig, and E. Ardonne, *Phys. Rev. B* **83**, 241302(R) (2011)
51. L. Andrew Wray, S. Y. Xu, Y. Q. Xia, D. Hsieh, A. V. Fedorov, Y. S. Hor, J. Cava, A. Bansil, H. Lin, and M. Z. Hasan, *Nature Physics* **7**, 32 (2011)
52. Q. Lin, C. X. Liu, C. K. Xu, X. L. Qi, and S. C. Zhang, *Phys. Rev. Lett.* **102**, 156603 (2009)
53. S. S. Pershoguba and V. M. Yakovenko, *Phys. Rev. B* **86**, 165404 (2012)
54. J. Henk, M. Flieger, I. V. Maznichenko, I. Mertig, A. Ernst, S. V. Ereameev, and E. V. Chulkov, *Phys. Rev. Lett.* **109**, 076801 (2012)
55. G. Kresse, and J. Furthmuller, *Comput. Mater. Sci.* **6**, 15-50 (1996)
56. G. Kresse, and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999)
57. L. Shen, M. G. Zeng, Y. H. Lu, M. Yang, Y. P. Feng, *Phys. Rev. Lett.* **111**, 236803 (2013)
58. S. V. Ereameev, Y. M. Koroteev and E. V. Chulkov, *JETP Letters* **91**, 387 (2010)

59. A. Sulaev, P. Ren, B. Xia, Q. H. Lin, T. Yu, C. Y. Qiu, S. Y. Zhang, M. Y. Han, Z. P. Li, W. G. Zhu, Q. Y. Wu, Y. P. Feng, L. Shen, S. Q. Shen, L. Wang, *AIP advances* **3**, 032123 (2013)
60. Z. G. Li, Y. Y. Qin, F. Q. Song, Q. H. Wang, X. F. Wang, B. G. Wang, H. F. Ding, C. van Haesendonck, J. G. Wang, Y. H. Zhang, G. H. Wang, *Appl Phys. Lett.* **100**, 083107 (2012)

Chapter 6. Future works

The physics of the topological insulator condensed matter state is currently one of the exciting research areas in physics. Not many experiments have been conducted in order to study the topological insulator based devices. In the later experiments we can continue our A-B effect measurements with the back gating. By using back gating it should be possible to control the quantum oscillations from surface states. Because by tuning the gate voltage we are also tuning the Fermi level of the surface states, at a given condition that the Fermi level passes through a Dirac point of the topological insulator surface state we can see higher mobility of the Dirac fermions thus the intensity of the oscillations from the A-B and AAS effects will be higher. The design of this experiment is the same as previous experiments performed to probe quantum oscillations with the difference having a back gating applied similar to the second experiment of ambipolar electric gate effect. The goal of these experiments is to employ external methods of manipulating the surface quantum oscillations. Although by fabricating thinner devices based on topological insulators, we can get the higher intensity of the quantum oscillations, but in our case we cannot keep fabricating nanoribbons thinner and thinner.

In the case of the Ag_2Te it is also important to perform ARPES analysis of this topological insulator material. Because theoretically it has been already proposed as topological insulator system, and in our works we have presented some experimental evidences of existence of surface states on Ag_2Te . ARPES results would confirm the exact shape of the electronic band structure of this material. We may able to obtain experimental evidence about the anisotropic Dirac cone shaped surface states. Also important informations about the bulk states and their influence on the surface states can be analysed. In fact successful outcome from this

experiment can push Ag_2Te into the topological insulator research as the main research material for the TI systems, because research society relies more on the ARPES results that can eliminate their doubts about the nature of the experimental results obtained by our work. Though our group is more in the electrical measurement research, ARPES can be done by collaboration with the experienced researchers on this field.

Spin-orbit interaction has been studied for a long time and different materials have been examined on their possible application for spintronics. But so far the research wasn't able to find suitable material for the spintronics, i.e. the electronics devices based on electron spin. This is the field that made topological insulator material systems as the exciting research field. One of the properties of the surface state of the topological insulators is the spin-momentum locked Dirac cone. The spin of the charge carriers is unaffected by the imperfections taking place on the surface. With the topological insulators that could provide high mobility at the surface states it's possible to realize very long spin relaxation length on the topological insulator based devices. With the successful results it can boost the development of the spintronics devices that can provide higher mobility thus better speed for the current technologies. One of the simple designs to analyse the spin properties like spin relaxation length, spin precession, spin coherence is shown in the Fig. 6.1. It consists of two metallic contacts (M) and two ferromagnetic contacts (F) on top of the topological insulator. Since the electrons on the surface states of topological insulator are polarized we must be able to detect the in some ways.

This is one of the simplest methods to detect the spin diffusion in the topological insulators. This configuration can serve as a usual resistivity measurement of the sample, but under applied external magnetic field the ferromagnetic contacts could be given certain magnetization alignment. The direction of the magnetic field is along the length of electrodes. Generally in the spin valve devices the input of the spin current into is done using

ferromagnetic contacts, but in our case we do not need spin input because the electrons are already polarized on the topological insulator surface states. Of course the big problem of these experiments will be still the bulk states interference. So in order to succeed in this experiment we must fabricate thin high quality devices. The current input is done using metallic contacts, spin current generated using these metallic contacts then later start to diffuse towards the ferromagnetic contacts that must be already magnetized. If the spin alignment of the electrons and the electrode magnetization are in the same direction then there is small voltage detected in the ferromagnetic contacts. But if the alignments of the electrode's magnetization and electron spin are different then voltage source would require spending some energy to detect the spin electrons. As for non-spin polarized electrons the voltage difference between those two scenarios will be zero. Thus in this way we can understand that surface electrons on the topological insulator are spin polarized.

The distance d between metallic and ferromagnetic contacts can be varied in different devices. The injected spin current has certain diffusion length which is destroyed by scattering and impurities. That is the reason why the measurement must be carried out on high quality samples and at low temperatures, where the scattering is significantly reduced. We can start with the small distance between metallic and ferromagnetic contacts and slowly increase the separation. After certain separation is achieved the spin signal would not be detected, because the distance is already larger than the diffusion length of the spin current. Also if the spin current is detected successfully using this method, then we can also experiment with the spin precession properties in the topological insulator systems. For this experiment the magnetic field must be perpendicular to the surface of the topological insulator. If the magnetic field and spin alignment are perpendicular to each other then we can observe the precession of the electron spin around the magnetic field. So when the electron spin precesses then we will have different spin alignment for different magnetic field

when electron arrives to ferromagnetic electrode. The ferromagnetic electrode can detect the changes in the spin alignment change and we can analyse how much electron has been affected by the magnetic field. It is also important to carry out these experiments under back gate voltage. Since the position of the Fermi level is generally shifted due to doping. By shifting the Fermi level we can achieve the highest spin diffusion and further discover how much the bulk states can affect the spin polarization of the surface states.

Figure 6.1. The topological insulator based spin valve device. It consists of two metallic contacts (M) and two ferromagnetic contacts (F) with magnetic field (B) along the electrodes.

The exciting spin properties of the topological insulators can be also studied using other techniques. Another interesting setup for the probing of the surface spin current is shown in Fig. 6.2 where the topological insulator is the H-shape with metallic and ferromagnetic contacts on the edges. This method is to detect the spin accumulation of the edges. In one of the legs of the topological insulator the current is input using metallic contacts. This current diffuses into another leg of the device, but since the spin current tends to travel along the edges it is possible to have spin accumulations on the edges of the second leg. Using ferromagnetic contacts we can measure the potential difference of this spin accumulation. If the current input is reversed then the electron spins will switch their accumulations points thus reversing the voltage difference between the ferromagnetic contacts. To fabricate this

kind of devices we may require techniques like Focused Ion Beam (FIB) to cut the devices into the desired shapes. Depending on the spin diffusion properties we can also switch the second leg with the materials that provide better spin propagation.

Figure 6.2. H-shaped topological insulator device designed to probe the spin accumulation of the edge spin currents.