

Photoemission Studies of Topological Insulators

Turgut Yilmaz

B. Sc., Ondokuz Mayıs University, 2007

M. Sc., University of Connecticut, 2014



A Dissertation

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Doctor of Philosophy

At the

University of Connecticut

2016

Photoemission Studies of Topological Insulators

Turgut Yilmaz, Ph.D

University of Connecticut, 2016

Topological insulators (TIs) attracted scientist due to its distinct electronic structure. TIs possess metallic surfaces due to strong spin orbit coupling, while the bulk shows the insulating behavior. On the surface of TIs topologically protected surface states obeys the massless Dirac equation, namely electron energy disperses linearly with respect its momentum. In addition, these surface states are protected against to backscattering because of the perpendicular locking of spin and momentum to each other.

The work presented in this thesis focused on the growth method of Bi_2Se_3 topological insulator under the ultra-high vacuum conditions and interaction of the topological surface states of Bi_2Se_3 with magnetic impurities and superconductors.

We presented x-ray photoemission spectroscopy (XPS) and angle resolved photoemission spectroscopy (ARPES) study to demonstrate high crystal quality of Molecular Beam Epitaxy (MBE) grown Bi_2Se_3 on Al_2O_3 (0001) substrate. We further supported our study by performing x-ray diffraction (XRD) and low energy electron diffraction (LEED) on Bi_2Se_3 thin film.

In addition, one of the interest on TIs is to introduce magnetic impurities into bulk and on the surface to break time reversal symmetry (TRS), which leads to open an energy gap at the Dirac point of TIs. Such experiment is important for experimental observation of Quantum Anomalous Hall effect. For this reason, XPS and ARPES study on Cr bulk and surface doped Bi_2Se_3 were presented in order to investigate magnetic impurity doping impact on the electronic and chemical

environment of Bi_2Se_3 . ARPES measurements revealed that Cr bulk doping opens an energy gap at the Dirac point without ferromagnetism, while gapless surface states are robust against Cr surface deposition.

Another interest on TIs is to obtain proximity induced superconductivity in order to open experimental avenue for possible experimental detection of long sought Majorana fermions. Therefore, we presented ARPES study on $\text{Bi}_2\text{Se}_3/\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (BSCCO) heterostructure in order to search for proximity induced superconductivity. In contrast to expectations, ARPES measurements do not show any sign of the proximity induced superconductivity in the thickness range from 0.5 quintuple layer of Bi_2Se_3 to 15 quintuple layer of Bi_2Se_3 .

Copyright by

Turgut Yilmaz



2016

APPROVAL PAGE

Doctor of Philosophy Dissertation

Photoemission Studies of Topological Insulators

Presented by

Turgut Yilmaz, B.Sc., M.Sc.

Major Advisor _____

Boris Sinkovic

Associate Advisor _____

Gayanath W. Fernando

Associate Advisor _____

Jason Hancock

University of Connecticut

2016

Acknowledgement

First and Foremost, I would like to thanks my mother Gulsum Yilmaz and my father Idris Yilmaz for their endless support and patience through my Ph.D life. I would also like to thanks my wife Rozita Ramli, her mother Zaharah Jusoh and (late) father Ramli Arshad.

I would like to extend my thanks to our little daughter Khadijah Gulsum Yilmaz for bringing happiness to our life.

I would also convey special thanks to my friends Sadullah Yildirim Murat Osmanoglu, Ahmet Teber, Yusuf Albayram, Omer Dis, Ozgur Oksuz, Hakan Gokmuharremoglu, Huseyin Yer and to many other for warm friendship.

I am also deeply grateful to my major advisor Dr. Boris for his guidance during the M.S. and Ph.D. program, and also friendly relationship trough the all these years.

I would like to extend my sincere gratitude to Dr. Hines and Dr. Budnick for always being supportive, and their cooperation on my projects. I will always remember and appreciate their unique approach to teaching and discussing.

Finally, I would like to acknowledge a graduate fellowship from the Republic of Turkey Ministry of National Education.

Table of Contents

1. Topological Insulators	1
1.1 Introduction	1
1.2 Quantum Hall effect	2
1.3 Quantum spin Hall insulators and topological insulators.....	7
1.4 Experimental realization of 2D topological insulators.....	15
1.5 Experimental realization of 3D topological insulators.....	17
1.6 Magnetic topological insulators	18
1.7 Majorana fermions in superconducting topological insulators	22
1.7.1 Theory of superconductivity	23
1.7.2 Current experiments towards superconducting TIs and the observation of Majorana fermions	26
1.8 References	29
2. Experimental Equipment and Techniques	32
2.1 Introduction	32
2.2 UHV Chambers and Conditions.....	32
2.3 Growth Method: Molecular Beam Epitaxy (MBE).....	34
2.4 Components of the experimental setup at the University of Connecticut (UCONN) and at the Brookhaven National Laboratory (BNL)	36
2.5 Photoemission Chamber.....	43
2.6 Photon Sources	45
2.6.1 X-ray gun	45
2.6.2 UV-Lamp	47
2.6.3 Synchrotron Radiation	48

2.7	Hemispherical Electron Analyzer	49
2.8	X-ray diffractometer.....	54
2.9	References	55
3.	Theories of Experimental Techniques.....	56
3.1	Introduction	56
3.2	Principles of Generating X-ray, UV and Synchrotron Radiation.....	56
3.3	Photoemission Spectroscopy.....	59
3.4	Theoretical Description of the Photoemission Process	63
3.5	Angle Resolved Photoemission Spectroscopy	67
3.6	ARPES: Current Applications.....	70
3.7	X ray photoemission spectroscopy (XPS).....	72
3.8	X-ray Diffraction.....	76
3.9	References	79
4.	Crystal and Electronic Structure of MBE grown Bi_2Se_3 Topological Insulator.....	80
4.1	Introduction	80
4.2	Experiment	83
4.3	Results	84
4.4	Conclusion.....	90
4.5	References	90
5.	Crystal and Electronic Structure of Cr Bulk Doped Bi_2Se_3	92
5.1	Introduction	92
5.2	Experiment	94
5.3	Results	96
5.4	Conclusion.....	109

5.5	References	110
6.	Impact of Cr Surface Deposition on the Chemical Environment and the Electronic Structure of Bi_2Se_3	112
6.1	Introduction	112
6.2	Experiment	114
6.3	Results	115
6.4	Conclusion.....	121
6.5	References	122
7.	Search for proximity induced superconductivity on $\text{Bi}_2\text{Se}_3/ \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ heterostructure	123
7.1	Introduction	123
7.2	Experiment	125
7.3	Results	126
7.4	Conclusion.....	142
7.5	References	143

List of Figures

Figure 1.1. Schematic representation of the Hall measurement sample. (b) Magnetic field dependence of the longitudinal component (ρ_{xx}) and the transverse component (ρ_{xy}) of the Hall resistance [3].	3
Figure 1.2. Continues energy spectrum under zero magnetic field ($\mathbf{B}=0$). (b) Quantized Landau levels in the presence of external magnetic field ($\mathbf{B}\neq 0$). (c) Localized and extended states in the QHE system [4].....	4
Figure 1.3.(a) Halperin's annular film used for electronic structure calculation [5]. (b) LLs as a function of position for annular film under the external magnetic field [5]. (c) Schematic representation of the QHE. Straight arrows indicate the current-carrying edges only in the one direction. Cyclotron motions of electrons under perpendicular magnetic field are represented by circles (d) Schematic representation of the single edge state in the band structure [10].....	5
Figure 1.4.(a) Four TRIM points in 2D and their reflection onto 1D as donated by Λ_1 and Λ_2 . (b) , (c) Electronic dispersion between two TRIM points for even and odd number of the Fermi level crossing, respectively [10].	10
Figure 1.5. Eight TRIM points in 3D and their reflection in 2D as donated by $\Lambda_1, \Lambda_2, \Lambda_3, \Lambda_4$ [14].	11
Figure 1.6. Fermi circles represented by shaded areas for a WTI and STI in (a) and (b) , respectively. Arrows indicates the electron spin direction. (c) Schematic representation a single Dirac cone enclosed by the Fermi circle in STI system [14].....	12
Figure 1.7.(a), (c) Schematic representation of spin filtered conducting edges and surfaces in 2D and 3D TIs, respectively. Different spins propagate in the opposite directions. Spins are represented with arrows. (b) Electronic structure of 1D TI shows 1D Dirac cone. Up and down arrows represent the direction of the spin. (d) 3D Dirac cone on the surfaces of 3D TIs. Black arrows represent to fully spin polarized surface state [17].	14
Figure 1.8.(a), (b) Schematic representation of QW below and above the critical QW thickness (6.5 nm), respectively [26]. (c) Electronic structure of normal state. (d) In the inverted region, bulk bands are inverted and topological surface state merges within the inverted bulk band gap [26]. (e) Experimental realization of the QSHI. Inset shows the temperature dependence of Hall resistance [13]. (f) Schematic representation of sample in the transport measurement [13].....	16

Figure 1.9. (a) Theoretical band structure of Bi_2Se_3 . [18] (b), (c) ARPES electronic structure of Bi_2Se_3 along the different direction in the Brillouin zone. Both spectra show Dirac like surface states [19]. (d) Theoretical band structure of Bi_2Te_3 [18]. (e) ARPES electronic structure of Bi_2Te_3 showing Dirac like dispersion of surface states [20] (f) Spin resolved ARPES measurement performed on Bi_2Te_3 [20].	18
Figure 1.10. (a) Schematic representation of the Hall measurement. (b) Hysteresis loop for ordinary Hall effect. (c) Hysteresis loop for anomalous Hall effect.	19
Figure 1.11. The QAHE in 5 QL $\text{Cr}_{0.15}(\text{Bi}_{0.1}\text{Sb}_{0.9})_{1.85}\text{Te}_3$ thin film. (a) Schematic representation of experimental geometry. (b) Magnetic field dependence of ρ_{yx} at different gate voltages (V_g). (c) Gate voltage dependence of $\rho_{yx}(0)$ and $\rho_{xx}(0)$. (d) Magnetic field dependence of ρ_{xx} . (e) Gate voltage dependence of the Hall conductance $\sigma_{xx}(0)$ and $\sigma_{xy}(0)$ [13].	20
Figure 1.12. (a), (b) Schematic representation of the Dirac cone in pristine sample and magnetically doped sample. (c), (d) ARPES measurements performed on pristine and Fe doped Bi_2Se_3 . Pristine sample shows clear Dirac like dispersion, while Fe doping opens an energy gap at the Dirac point [31].	21
Figure 1.13. Schematic drawing of lattice distortion in superconductors. Black solid spheres represent the positively charged atom cores and gray small balls are the electrons. Two electrons together represent the Cooper pair formed through lattice distortion.	24
Figure 1.14. Superconducting proximity effect. SC and NM represents the superconductor and normal metal respectively. B is magnetic field applied in plane of the sample to detect proximity effect.	25
Figure 1.15. Resistivity of $\text{Cu}_{0.12}\text{Bi}_2\text{Se}_3$ as a function of temperature. Lower inset shows the superconducting transition temperature is 3.8 K [39].	26
Figure 1.16. (a) A schematic representation of molecular beam epitaxial grown Bi_2Se_3 film on s-wave superconductor NbSe_2 . (b) ARPES 2D intensity of 3 quintuple layer of Bi_2Se_3 grown on NbSe_2 taken with 50 eV photon energy at 12 K. (c) Temperature dependence of energy dispersive curves taken with 50 eV photon energy at $-k_1$ as indicated in (b) [47].	28
Figure 1.17. (a) A schematic illustration of $\text{Bi}_2\text{Te}_3/\text{NbSe}_2$ heterostructure. (b) Single vortex mapping at zero-bias on 5QL Bi_2Se_3 on NbSe_2 at 0.4 K and 0.1 T. (c) Density of state measurement by STM on the vortex in (b) [49].	29
Figure 2.1. Schematic illustration of Molecular Beam Epitaxial (MBE) chamber.	35

Figure 2.2. Schematic drawing of the top view of experimental setup at University of Connecticut. Evaporators in the MBE chamber are located at the bottom of the chamber (not shown here). ..	36
Figure 2.3. Schematic drawing for top view experimental setup at U5 beam line at Brook Haven National Laboratory.	37
Figure 2.4. Schematic drawing of Load-Lock Chamber.	38
Figure 2.5. Schematic drawing of the top view of the MBE chamber used at UCONN and BNL. Evaporators are located at the bottom of the chamber.	39
Figure 2.6. Schematic drawing of evaporators used in this thesis. (a) Resistive heating evaporator, (b) e-beam heating evaporator.	40
Figure 2.7.(a), (b) Evaporation rates of Bi and Se sources as a function of temperature. (c) Cr evaporation rate as a function of emission current at 1.8 kV high voltage.	42
Figure 2.8. Schematic drawing of the sample plate and manipulator sample plate holder. In most of the case, one side of the filament is connected to power supply and other side is grounded... ..	42
Figure 2.9. Top view of the photoemission chamber at UCONN. Green and blue sample orientation is corresponding to XPS for core-level photoemission spectroscopy and ARPES for electronic structure analyses, respectively. BNL photoemission chamber has similar setup but a synchrotron radiation is used for core-levels and ARPES experiments.	44
Figure 2.10. Schematic drawing of x-ray gun and close-up view of the head used in core-level spectroscopy at UCONN.	46
Figure 2.11. Schematic drawing of the UV-lamp. Ultra-high vacuum side is shown with and rectangular. Gas inside the discharge section	47
Figure 2.12. Technical representation of the synchrotron radiation facilities. According to the purposes, different experimental stations are setup at the end of each beam line, such as, ARPES station [10].	49
Figure 2.13. Schematic drawing of the hemispherical electron analyzer.	51
Figure 2.14. 3D view of modern electron analyzer.	52
Figure 2.15. Drawing of MCP detector and single channel [11].	53
Figure 2.16. Schematic drawing of x-ray diffractometer.	54
Figure 3.1. Schematic representation of x-ray radiation generation.	56
Figure 3.2. Power versus photon energy of synchrotron radiation.	59

Figure 3.3. Schematic illustration of interaction of the light and core-level electrons producing the photoelectron.....	60
Figure 3.4. Schematic representation of the photoemission process. The left side of the figure shows the density of the electrons inside the solid as a function of the binding energy. The recorded photoemission spectra as a result of photoemission process is shown in the right side of the figure for XPS and ARPES [2].....	61
Figure 3.5. Three step model representation of photoemission process [4]	62
Figure 3.6. Universal curve for electron mean free path as a function of their kinetic energies [3].	63
Figure 3.7. Schematic representation of photoemission geometry of $dx^2 + y^2$ orbit for s and p polarized light with respect mirror plane [19].	66
Figure 3.8.(a) Band structure of Ag along the [111] direction. Direct transitions are represented by vertical arrows for different photon energies. (b) Normal emission spectra from Ag (111) taken with 7, 8, and 9 eV photon energies. Dashed horizontal line represents the zero intensity [18]..	67
Figure 3.9.(a) 3D representation of components of the photoelectron momentum in the vacuum. (b) Parallel and perpendicular momentum of the photoelectron inside the solid and the vacuum. At the interface of the solid and the vacuum, parallel component of the photoelectron momentum is conserved.....	68
Figure 3.10. ARPES measurement taken from cleaved Bi_2Se_3 with 18 eV photon energy. Upper panel and right panel show the MDC and the EDC along the red and blue line, respectively.	70
Figure 3.11.(a) Fermi surface of $\text{FeTe}_{0.6}\text{Se}_{0.4}$ measured at 25 K. (b) Temperature dependence of EDC taken at $\phi=0^\circ$ at the Fermi level [11].	72
Figure 3.12. Common line shapes used in XPS peak fitting. DS line shape is drawn for different asymmetry parameter (αDS). G and L represent the Gaussian and Lorentzian line shapes, respectively. [6].....	74
Figure 3.13. XPS peak fitting background line shapes [5].	75
Figure 3.14. Diffraction of x-rays from atomic planes [17].....	77
Figure 4.1.(a) Schematic representation of the band inversion in Bi_2Se_3 . (b) Schematic illustration of the bulk conduction band and the bulk valence band in the normal and inverted states. Plus, and minus represent the band parities.....	81
Figure 4.2.(a) Crystal structure of Bi_2Se_3 . (b) Side view of the crystal structure [1].	82

Figure 4.3.(a) XRD pattern of 22 QL Bi_2Se_3 . Scans are taken with a Cu anode ($\lambda = 1.54 \text{ \AA}$). (b) LEED pattern of 22 QL Bi_2Se_3 obtained with 174 eV electron energy.....	84
Figure 4.4. XPS study of the MBE grown 22 QL of Bi_2Se_3 thin film on $\text{Al}_2\text{O}_3(0001)$ substrate. (a) The survey XPS spectrum 22 QL of Bi_2Se_3 . (b) Bi 4f and (c) Se 3d. All the spectra were recorded at the room temperature with 1485.6 eV radiation. Purple and cyan colored lines represent the linear combination of Gaussian and Lorentzian fitting line shapes. Brown line represents the Shirley type background.	85
Figure 4.5. Electronic structure of 10 QL Bi_2Se_3 taken with 21.2 eV photon energy along the Γ -M direction at the room temperature. Thick orange line represents to surface states and dashed green lines indicate the bulk bands. Fermi level is shown by dashed yellow line.....	86
Figure 4.6.(a-e) Thickness dependence ARPES 2D intensity of Bi_2Se_3 . Solid red lines represent the evolution of gapless surface state. The dashed yellow lines and the solid red lines indicate the Rashba states and the surface states, respectively. Spectra were collected along with 21.2 eV photon energy the along the Γ -M direction at the room temperature.	87
Figure 4.7.(a) ARPES 2D intensity of 22 QL of Bi_2Se_3 thin film. (b) Wider energy map of the electronic structure of Bi_2Se_3 . (c) Energy dispersive curves (EDCs) at different $k_{\parallel}$, (d) EDC at the Γ (000) point. Thick white line represents the Fermi level, and arrows in (d) show the bulk bands. ARPES spectra were recorded along the Γ -M direction with 21.2 eV photon energy and at the room temperature.	89
Figure 5.1.(a), (b), (c) are the electronic structure of Bi_2Se_3 , Cr doped Bi_2Se_3 and Co doped Bi_2Se_3 , respectively [3].....	93
Figure 5.2. XRD patterns for pristine and Cr doped Bi_2Se_3 films. Cr concentrations are written on the right side of the patterns. All the sample have the same thickness of 25 QL. XRD patterns were recorded with Cu x-ray source.	96
Figure 5.3. Core-level peaks of Bi 4f, Bi 5d, Se 3d and Cr 3p taken from $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$. Spectra were recorded with Al $K\alpha$ x-ray source at the room temperature and at 45° emission angle with SES-100 electron analyzer at UCONN.....	97
Figure 5.4.(a-d) ARPES 2D intensity plots as a function of energy and momentum from pristine sample and Cr doped samples for $x=0.05, 0.16$ and 0.22 . Solid green line represents the topological surface states and DP stands for the Dirac point. (e-g) Corresponding 2D plots in wider energy range to observe the bulk bands. ΔD is the energy gap at the Dirac point. Spectra were recorded at	

the room temperature with 21.2 eV He-I radiation source along the Γ -M direction with SES-100 electron analyzer at UCONN.	98
Figure 5.5.(a), (b) ARPES 2D intensity of $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ at the room temperature and at 100 K, respectively. (c), (d) ARPES 2D intensities of $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$ at the room temperature and at 100 K, respectively. Spectra were recorded along the Γ -M direction with He-I light source and SES-100 electron analyzer at UCONN. Red lines indicate the energy gap.	100
Figure 5.6. Temperature dependent core-level spectra of Bi 5d, Se 3d and Cr 3p obtained from $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$. The data were taken with Al $K\alpha$ x-ray source and SES-100 electron analyzer at UCONN.	101
Figure 5.7.(a-e) ARPES 2D intensities along the Γ -M direction for Cr content of $x=0, 0.05, 0.09, 0.16$, and 0.22 . The solid blue line and yellow lines represent the Dirac point (DP) and surface states, respectively in (a). The dashed white lines represent the Fermi level. Spectra were recorded at the room temperature with 52 eV photon energy at NSLS/BNL. (f-k) Corresponding EDC for each ARPES 2D intensity, respectively. (i) ΔD as a function of Cr content. Solid black line is the fitting. ΔD is measured based on Reference 10. (j) Momentum dispersive curves (MDCs) at the Fermi level obtained from the ARPES (Cr contents are indicated at the right of MDCs).	102
Figure 5.8.(a), (b) Temperature dependent ARPES 2D intensities obtained from $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$ sample the Γ -M direction recorded with 52 eV photon energy at the room temperature and 100 K respectively at NSLS/BNL. (c) and (d) are corresponding EDCs.	104
Figure 5.9.(a), (b) High resolution core-level spectra of Bi 5d and Se 3d respectively. Cr concentration is written on the left side of images. Spectra were recorded with 104 eV photon energy at the room temperature at NSLS/BNL.	105
Figure 5.10.(a), (b) In-plane magnetic properties of 46 QL Bi_2Se_3 and $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$. (c) Magnetic hysteresis loop for 46 QL $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ film at 5.0 K after subtracting the diamagnetic background curve obtained at $T = 5.0$ K in (b) . (d) Zero-field-cooled/field-cooled curves for 46 QL $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ film in a magnetic field of 50 Oe applied in the sample plane.	106
Figure 5.11.(a), (b) Out-of-plane magnetic properties of the 46 QL Bi_2Se_3 and $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$. (c) magnetic hysteresis loop for 46 QL $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ film at 5.0 K after subtracting the diamagnetic background curve obtained at $T = 5.0$ K in (b) . (d) Zero-field-cooled/field-cooled curves for 46 QL $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ film in a magnetic field of 500 Oe applied along the sample normal.	108

Figure 6.1.(a) ARPES 2D intensity of Bi_2Se_3 . BCB, BVB and SSB represent bulk conduction band, bulk valance band and surface state band, respectively. (b) ARPES 2D intensity of $(\text{Bi}_{0.99}\text{Mn}_{0.01})_2\text{Se}_3$ shows the Fermi level inside the surface Dirac gap. Inset: close-up of the dispersion in the vicinity of the Fermi level. (c) The energy dispersive curve (EDC) along the white dashed line in (b) and taken from the Au reference showing 7 meV energy gap. Spectra were recorded at 10 K with 48 eV photon energy [7].	113
Figure 6.2. ARPES 2D photoemission intensity plots as a function of energy and momentum from pristine sample and Cr deposited on the surface of Bi_2Se_3 . Spectra were recorded at the room temperature with 21.2 eV He-I radiation source at UCONN with SES-100 electron analyzer. $k_{\parallel}$ direction is along the Γ -M direction.	115
Figure 6.3.(a) EDC at $\Gamma(000)$ for different thickness of the Cr on the surface of Bi_2Se_3 . Dashed black lines represent the binding energy of the Dirac Point. Two quantum well states are attributed as QW1 and QW2. (b) Binding energy of the Dirac point as a function of Cr thickness in monolayer (ML). EDCs are obtained from the ARPES measurements presented in Figure 6.2.....	116
Figure 6.4.(a), (b) ARPES 2D intensities of pristine and 0.7 ML Cr surface doped sample at the room temperature. (c) ARPES 2D intensity of 0.7 ML Cr surface doped sample at 15 K. Spectra were recorded with 52 eV photon energy along the Γ -M direction at NSLS/BNL.	117
Figure 6.5.(a) ARPES 2D intensity of 0.7 ML Cr surface doped Bi_2Se_3 at 15 K with 21.2 eV photon energy along the Γ -M direction. (b) EDC at $\Gamma(000)$ point. Dashed red lines represents the QWS.....	118
Figure 6.6. Core spectra of Bi 5d, Se 3d and Cr 3p as a function of Cr coverage levels are given in (a), (b) and (c) respectively. Thick green lines represent the linear combination of Lorentzian and Gaussian fitting line shape, and thick brown line is Shirley type of background. Cr amount is written on the right sides of spectra. Core-levels recorded at the room temperature with 104 eV photon energy at NSLS/BNL.	119
Figure 7.1.(a) ARPES measurement of Bi_2Se_3 grown on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (BSCCO) superconducting substrate. (b) Energy dispersive curve (EDC) taken from the left surface states along the dashed lines in (a), and black line represents the reference EDC taken from Au. (c) Temperature dependence of the superconducting energy gap. ARPES and EDCs are taken with 50 eV photon energy [17].	124

Figure 7.2.(a) Fermi surface of BSCCO substrate after annealing at 420 K red inset circle is the fermi surface of 10 QL Bi_2Se_3 . **(b), (c)** ARPES 2D intensity at the nodal and anti-nodal region, respectively. **(d)** EDCs at the nodal and the antinodal region indicated with dashed red line and solid black line in (a), respectively Measurements were recorded at 30 K with 30 eV photon energy.

..... 128

Figure 7.3. Structure of a Bi_2Se_3 film on a BSCCO substrate. **(a)** Schematic view of the studied structures. **(b)** μ -LEED image of a 10 QL Bi_2Se_3 film at 350 K. **(c)** μ -LEED image at $T=750$ K. **(d)** A real-space, dark-field LEEM image obtained from a diffraction spot corresponding to one of the domains. Bright features, representing the domains that contribute to the chosen diffraction spot. Images were taken at 20 and 18 eV in diffraction and real-space imaging modes, respectively.

..... 129

Figure 7.4. Core-level spectra of Bi 5d and Se 3d taken from 10 QL Bi_2Se_3 at 30 K with 104 eV photon energy..... 130

Figure 7.5.(a) The in-plane components of spin polarization of 10 QL Bi_2Se_3 grown on BSCCO substrate. Data recorded at 30 K with 52 eV photon energy. **(b)** Schematic representation of helical spin polarization on the surface of Bi_2Se_3 . Black circle and blue arrows represent Fermi surface and spin directions, respectively. A and B represent points where the spin polarized ARPES was performed. 132

Figure 7.6.(a) ARPES 2D intensity of 15 QL Bi_2Se_3 grown on BSCCO substrate. Spectra is recoded at 30 K with 52 eV photon energy along the Γ -M direction. Left and right topological surface states are donated as TSSL and TSSR respectively. **(b)** leading fermi edges along the dashed line in (a) for TSSL and TSSR represented with red and blue solid lines respectively with Au fermi reference EDC (yellow solid line. Black solid line in (b) is averaged EDC over the momentum space..... 133

Figure 7.7.(a) ARPES 2D intensity of 15 QL Bi_2Se_3 taken at 30 K with 63.5 eV photon energy along the Γ -M direction. QWS and the TSSs are represented with dashed red and green line respectively. Fermi level crossing points of the QWS and surface states are represented with black and SSL, QWL, SSR, QWR are donated for the left and right TSSs and quantum well states respectively. **(b)** Fermi surface mapping of 15 QL Bi_2Se_3 that shows the characteristic circular fermi surface of Bi_2Se_3 . **(c)** EDCs curves along the dashed lines in (a) with Au reference Fermi edge. **(d)** Integrated EDC along the momentum region..... 135

Figure 7.8. Thickness dependence electronic structure of Bi_2Se_3 . (a), (b), (c) ARPES 2D intensities of 10 QL, 6 QL, 3 QL Bi_2Se_3 taken at 30 K with 52 eV photon energy along the Γ -M direction. (d), (e), (f) corresponding EDCs left and right side of the Dirac cone as pointed on the top of each ARPES on the left side of panel.....	137
Figure 7.9. (a), (b), (c) Integrated EDCs of ARPES 2D intensities for 10 QL, 6 QL and 3 QL Bi_2Se_3	138
Figure 7.10.(a) ARPES 2D intensities of 1 QL Bi_2Se_3 on BSCCO substrate recorded at 30 K with 20 eV photon energy along the Γ -M direction. (b) Corresponding energy dispersive curves at momentum region indicated with dashed lines in (a).	139
Figure 7.11.(a), (b) ARPES 2D intensity of 1 QL $\text{Bi}_2\text{Se}_3/\text{Bi}_2/\text{BSCCO}$ heteroturtucture takenat 30 K with 52 eV and 17 eV photon energies along the Γ -M direction, respectively. Dashed red and solid green line represent the bulk and surface states respectively. (c), (d) , EDCs along the left and right surface and quantum well states with integrated energy EDCs along the momentum region.	140
Figure 7.12.(a) A schematic representation of a sub-QL Bi_2Se_3 film. (b) ARPES 2D intensity of a ~ 0.5 QL Bi_2Se_3 film on a BSCCO substrate at 30 K with 52 eV photon energy along the Γ -M direction. The precursor of TSS is visible near the Γ point. (c) A characteristic EDC corresponding to the spectrum shown in (b) (red line) and a spectrum from an Au reference (black line). The EDCs from the film do not show any k dependence.	141

List of Tables

Table 2.1. Classification of the vacuum regions and the corresponding pressure ranges in torr .	33
Table 2.2. The most common anode elements used in x-ray guns with spectral line and corresponding photon energies	46
Table 2.3. Most common gases used in UV discharge lamps with spectral line and corresponding photon energies.	48
Table 5.1. Formation energies for Cr and Co atoms for different lattice sites, and corresponding magnetic moments (arrows indicate the alignment of magnetic moment) [3].	93
Table 5.2. Binding Energies (BE) of spectral lines taken from the $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$	97

1. Topological Insulators

1.1 Introduction

In this chapter, I will give a detailed overview of theoretical and experimental literature that leads the birth of topological insulators (TIs) which is the main subject of this PhD dissertation. The birth of TIs started with a remarkable discovery in condensed matter physics that is the quantum Hall effect [3]. The quantum Hall system is the quantized version of ordinary Hall conductance originating from the charge conduction only by the sample edges [5]. The difference between the quantized Hall system and the ordinary Hall system is the only matter of the bulk topology leading topologically classify the quantum Hall system with a topological invariant number, called D. J. Thouless, M. Kohmoto, M. P. Nightingale and M. den Nijs (TKNN) invariant or Chern number [6-7].

What directs studies towards the discovery of TIs is that the experimental difficulties for the observation of the quantum Hall effect, such as high magnetic field and very low temperature [22]. This guides scientists to search for new materials showing similar features with the quantum Hall system without external magnetic field [22, 8]. These materials are known as the quantum spin Hall insulators (QSHIs), which are the first real example of 2D TIs [8]. QSHIs are also topologically distinct from other materials and are classified by topologically invariant number, called Z_2 to differentiate them from the other materials [9]. The QSHI and the quantum Hall system share remarkable similarities in terms of having conducting edges at the sample boundaries while the interior of these materials are insulating. In QSHIs, however, instead of magnetic field, strong spin-orbit interaction is the driving force behind the formation of the conducting edge states. Unlike the quantum Hall system, these edge states are spin filtered [8]. In addition, in QSHIs, strong spin-orbit interaction leads a band inversion between the bulk conduction band and bulk

valance band. The inverted bulk bands are separated with an energy gap where topological surface states are located.

TIs have been experimentally discovered on a number of materials by transport measurements and angle resolved photoemission spectroscopy (ARPES) [13,16,18]. After experimental realizations of these materials, tremendous effort has been made for possible uses of these materials in the technology and experimental observation of various exotic quantum phenomena. For example, they are important candidates for experimental observations of long sought Majorana fermions in superconducting TIs, and the quantum anomalous Hall effect in magnetic TIs [23-28].

Each of these fundamental concepts of TIs mentioned above will be introduced in the following sections step by step in order to give a better understanding of physics behind TIs. The order of the topics is in the historical sequence so that the reader can easily keep track of the scientific progress up to present. We then extend our discussion to experimental realization of TIs and their possible use in the new discoveries in condensed matter physics.

1.2 Quantum Hall effect

Indeed, the path to TIs started with the observation of ordinary Hall effect. This effect states that, if a current-carrying conducting plate is placed in a perpendicular magnetic field, a voltage difference develops across the plate. This voltage (Hall voltage) difference originates from the traveling of electrons from one side of the plate to another due to the applied magnetic field. This effect is known as ordinary Hall effect, which was first observed by Edwin Hall in 1879 [2].

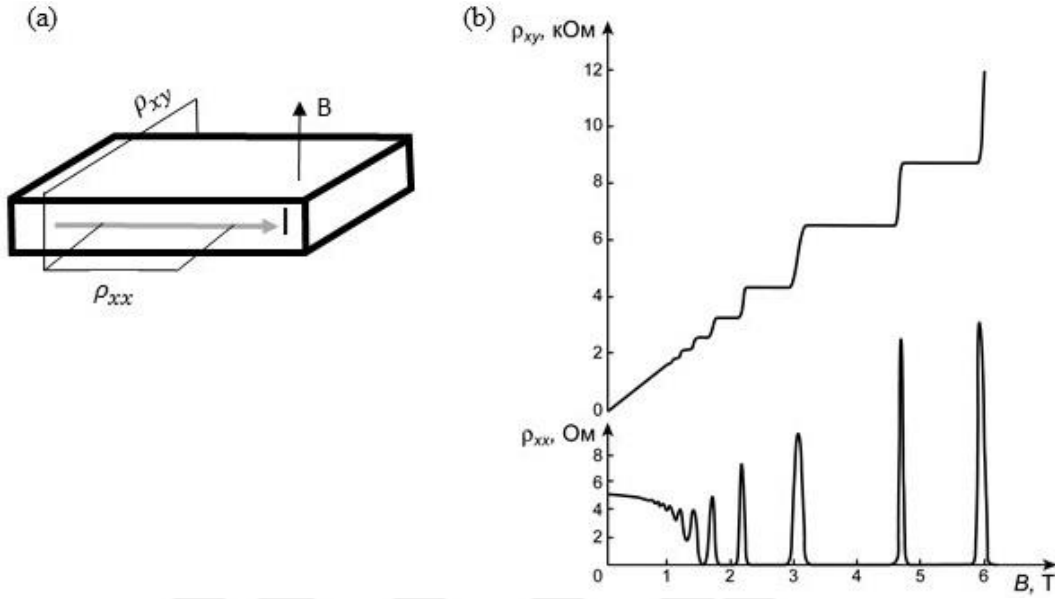


Figure 1.1. Schematic representation of the Hall measurement sample. **(b)** Magnetic field dependence of the longitudinal component (ρ_{xx}) and the transverse component (ρ_{xy}) of the Hall resistance [3].

Almost 100 years after Edwin Hall's discovery, a remarkable observation was made by Von Klitzing and his colleagues in 1980 [3]. They showed the quantized version of the Hall effect on Si/SiO₂ field effect transistor, which has 2D electron gas at the interface [3]. Under the strong magnetic field, they experimentally presented step-like behavior of transverse component (ρ_{xy}) the Hall resistance with plateaus where the longitudinal component of the Hall resistance becomes 0 ($\sigma_{xx} = 0$) as seen in Figure 1.1. This observation shows the quantized form of the Hall conductance σ_{xy} in fundamental units of $\frac{e^2}{h}$ and it is given by [3]:

$$\sigma_{xy} = n \frac{e^2}{h} \quad n = 1, 2, 3, \dots \quad (1.1)$$

where e is electron charge and h is Planck constant and n is filling factor of Landau levels (LLs).

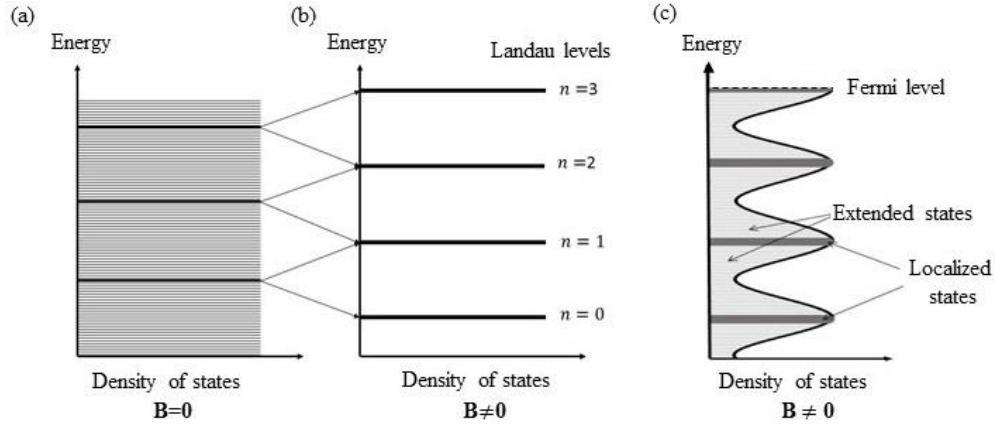


Figure 1.2. Continues energy spectrum under zero magnetic field ($B=0$). **(b)** Quantized Landau levels in the presence of external magnetic field ($B \neq 0$). **(c)** Localized and extended states in the QHE system [4].

After this outstanding discovery, one of the first attempts to explain the QHE was made by Laughlin in 1981 [4]. He suggested that the current-carrying extended states and the insulating localized states were formed inside the broadened LLs by disorder (Figure 1.2(c)). As seen from the Figure 1.2(c), the extended states are located at the center of the LLs, and connected to each other with the localized states. This approach models the QHE based on the number of the extended states below the Fermi level. By increasing the electron density, different LLs can be filled. When the Fermi level is located within the localized states, the number of the extended states will not change. Therefore, the Hall resistance is also unchanged, which corresponds to the Hall plateau. When the Fermi level passes the next set of extended states, there is a finite conductance indicating transition to the next plateau.

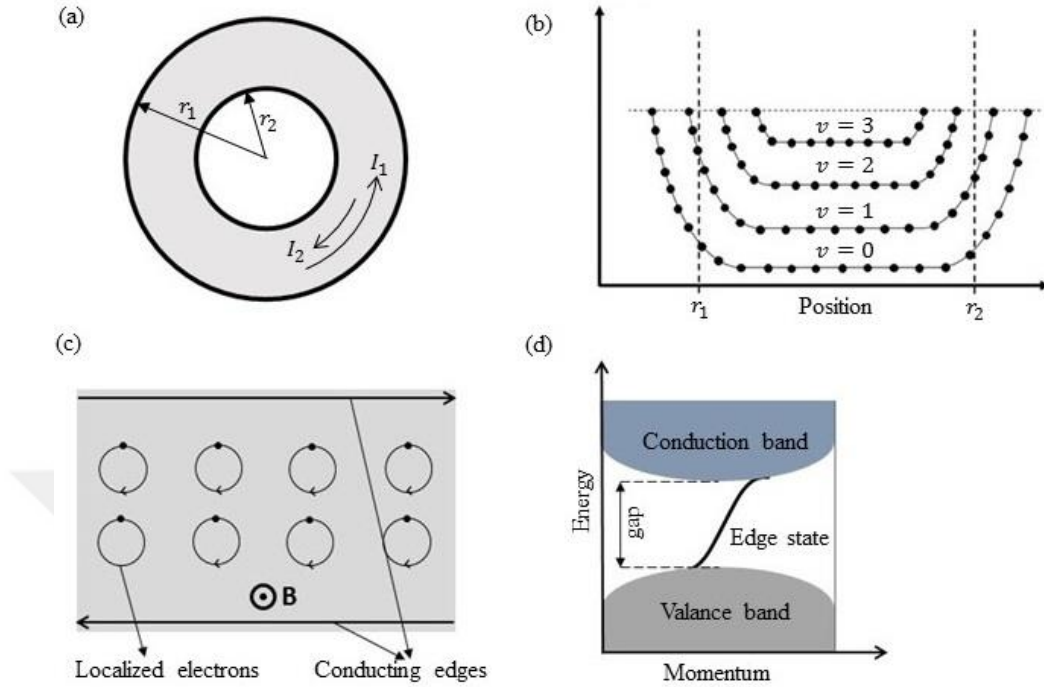


Figure 1.3. (a) Halperin's annular film used for electronic structure calculation [5]. (b) LLs as a function of position for annular film under the external magnetic field [5]. (c) Schematic representation of the QHE. Straight arrows indicate the current-carrying edges only in the one direction. Cyclotron motions of electrons under perpendicular magnetic field are represented by circles (d) Schematic representation of the single edge state in the band structure [10].

In 1982, another important contribution made by Halperin for understanding the physics behind the QHE [5]. He considered a thin film with annular shape as shown in Figure 1.3(a). Solution to the Schrodinger equation at the boundaries of the sample showed that LLs are bent upward crossing the Fermi level only at the sample boundaries (Figure 1.3(b)). In this model the Fermi level has to be in the middle of the LLs allowing the band crossing only at the sample boundaries. This shows that the conduction only occurs through the edges while the rest of the sample shows insulating behavior as shown in Figure 1.3(c). By creating a voltage difference between the sample edges, the Fermi level in each edge can be located at different energies. This results in electrical conduction only by the sample edges. These edges carry current in the opposite direction to each other making a single channel for charge transfer. This also confirms that

backscattering of the electrons are forbidden because electrons can flow only in one direction at the edges as shown with straight thick arrows in Figure 1.3(c).

In the journey to understand the QHE, more advanced work was done by D. J. Thouless, M. Kohmoto, M. P. Nightingale and M. den Nijs (TKNN) in 1982 [6]. After the discovery of the QHE, scientist asked: “What is the difference between the ordinary Hall effect and the QHE?”. The answer involved the matter of the bulk band topology, first shown by TKNN [6-7]. They derived the Hall conductance based on the Kubo formula for the non-interacting electron system moving in x - y plane under a perpendicular magnetic field. In their model, the Hall conductance was given by [21]:

$$\sigma_{xy} = \frac{e^2}{h} \oint \frac{dk}{2\pi} \Delta_k \theta(k) \quad (1.2a)$$

$$= \frac{e^2}{h} \nu \quad (1.2b)$$

where “ ν ” is well know TKNN integer, $\theta(k)$ is the total phase factor between the opposite points in the rectangular Brillouin zone, e is the electron charge, h is the Planck constant and k is the wave vector. The integral is over the number of total changes around the boundary of the rectangular magnetic Brillouin zone [21]. Therefore, the integral must give the integer multiple time of 2π , which is the phase acquired in one full turn around the Brillouin zone. This shows the quantized version of the Hall conductance. TKNN integer is in fact the topological invariant, and equivalent to first Chern class of a $U(1)$ fiber bundle on a torus [7, 21], as first showed by Avron, Seiler and Simon in 1983 [7]. Since the Bloch wave function is periodic as a function of the wave vector, the rectangular Brillouin zone is equivalent to 2D torus $\mathcal{T}^2$ [7,21]. This forms the fundamental connection between the QHE and the topology and shows that materials can be classified topologically by an invariant number so that the band insulators and the quantum Hall

states are characterized by TKNN invariants $\nu = 0$ and $\nu \neq 0$, respectively. In addition, quantization of the Hall conductance is insensitive to the experimental consideration such as material shape and the imperfections in the material since it only depends on the topological nature of the bulk bands [21].

Topological classification of the gapped band structure leads to an important consequence at the interface of materials where the topological invariance has to change. Changes in the topological invariance happens through the topological phase transition, which can only occur by gap closing. We can consider the interface between the quantum Hall state ($\nu = 1$) and vacuum ($\nu = 0$) as an example. The energy gap has to vanish at the interface in order to allow the topological phase transition to take place. This guarantees the existence of conducting edge states located within the bulk band gap on the edge of the quantum Hall system (Figure 1.3(d)), and is known as bulk-boundary correspondence [17].

In the above discussions, we introduced “the topology” and “the edge state” terms used in the QHE and are important concepts to understand the physics behind TIs. In the following section, we introduce another generation of the quantized Hall effect, called the quantum spin Hall effect, which are the first example of the TIs.

1.3 Quantum spin Hall insulators and topological insulators

Experimental observation of the QHE requires very low temperature and high magnetic field, which make these materials hard to use in the technology. This leads an important question: “Is it possible to obtain conducting edge states up to room temperature without magnetic field?”. The answer came from Kane and Male in 2005 [8]. They showed the presence of the spin filtered conducting edges in the 2D graphene without magnetic field. In this material, strong spin-orbit

interaction opens an energy gap in the bulk, while the topology of the band structure guarantees the spin polarized conducting edges only at the sample boundaries [8]. The energy spectrum of these surface states is characterized by the massless Dirac equation given by $E = \mp \hbar k v$ where k and v are electron momentum and velocity, respectively [8]. These systems are called QSHIs, which are the first real example of 2D TIs. In the QSHI, the number of the left and the right moving electrons are equal to each other resulting in zero net charge current. However, the spin current is non-vanishing and is equal to $(e^2/4\pi)(n_{\uparrow}-n_{\downarrow})$ where $n_{\uparrow}$ and $n_{\downarrow}$ are the number of spin up and spin down edge states, respectively [15].

In contrast to the QHE, time reversal symmetry (TRS) is not broken in a QSHI system, since there is no magnetic field. Therefore, inversion symmetry ($\varepsilon_{\uparrow}(k) = \varepsilon_{\uparrow}(-k)$), and TRS ($\varepsilon_{\uparrow}(k) = \varepsilon_{\downarrow}(-k)$) yield well know spin degeneracy in these systems, called the Kramers spin degeneracy [10]:

$$\varepsilon_{\uparrow}(k) = \varepsilon_{\downarrow}(k) \quad (1.3)$$

where $\uparrow$ and $\downarrow$ represents the spin-up and spin-down states. Spin orbit interaction leads to spin splitting of states away from the high symmetry points of the Brillouin zone. Therefore, Kramers spin degeneracy can exist only at the special points in the Brillouin zone called time reversal invariant momenta (TRIM) points [14-15]. In addition, since the states are occupied in the momentum k and $-k$ with opposite spins by TRS, the backscattering of the electrons, which requires spin flipping, are forbidden.

Since TRS is not broken in the QSHI systems, the TKNN invariant number must be zero. However, vanishing the TKNN integer ν corresponds to the band insulator. Hence, a new topological invariant number is needed for topological classification of QSHIs. This topological

invariant number was introduced by Kane and Male [9]. This invariant number is called Z_2 topologically invariant, ν , which can be computed for 2D system by [14]:

$$(-1)^\nu \equiv \prod_{\alpha=1}^4 \delta_\alpha \quad (1.4a)$$

$$\delta_\alpha \equiv \frac{Pf[w(\Gamma_\alpha)]}{\sqrt{\det[w(\Gamma_\alpha)]}} = \pm 1 \quad (1.4b)$$

where $w(\Gamma_\alpha)$ is a unitary matrix. In the presence of the inversion symmetry, the Pfaffians (Pf) can be expressed in terms of the parity eigenvalue ξ_{2n} of the occupied Bloch states. Then Equation 1-4b for $2N$ occupied states can be written as the product of the eigenvalues over the Kramers pairs:

$$\delta_\alpha \equiv \prod_{n=1}^N \xi_{2n} \quad (1.5)$$

Time reversal polarization (TRP) is defined as $\pi_\alpha \equiv \delta_{\alpha 1} \delta_{\alpha 2} = \pm 1$ [14]. Since δ_α can have the values of +1 or -1, ν can be either zero corresponding to the band insulator or 1 corresponding to the QSHI in 2D system.

In 2D system, there are four TRIM points defined by $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$ and their projection in 1D are Λ_1 and Λ_2 (Figure 1.4(a)). There are two possible ways of constructing the Kramers degeneracy at Λ_1 and Λ_2 depending on the TRP of TRIM points, which reflects the topology of the bulk bands. In the first case, surface states show zig-zag behavior by connecting the bulk conduction band and the bulk valance band and forming the Kramers degeneracy at Λ_1 and Λ_2 TRIM points (Figure 1.4(b)). In this case, surface states cross the Fermi level an odd number of times.

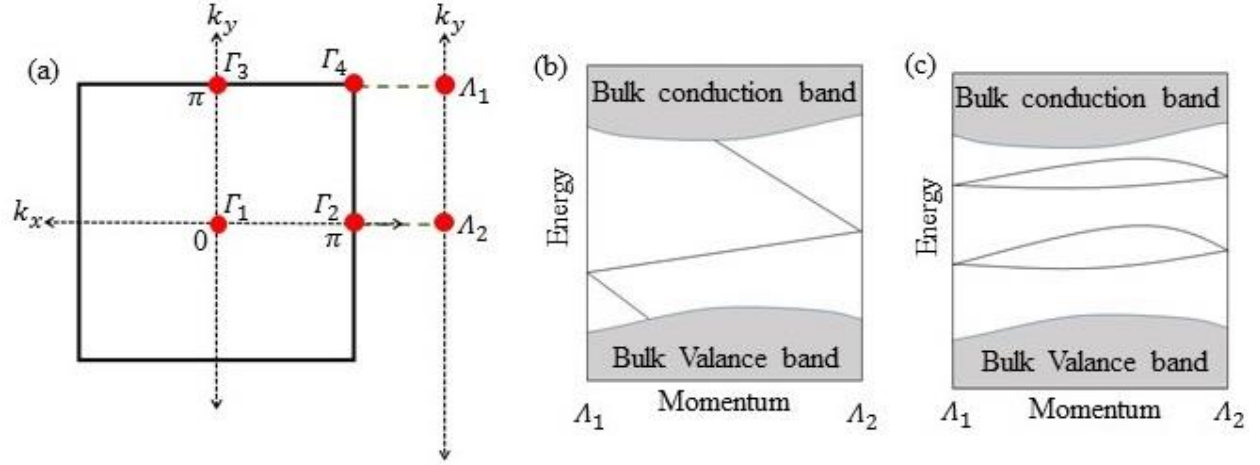


Figure 1.4.(a) Four TRIM points in 2D and their reflection onto 1D as donated by Λ_1 and Λ_2 . (b), (c) Electronic dispersion between two TRIM points for even and odd number of the Fermi level crossing, respectively [10].

In this electronic structure, surface state cannot be removed by manipulating the Fermi level within the bulk band gap. There is always an odd number of the Fermi level crossing by the surface states. This corresponds to the TRP of $\pi_a \pi_b = -1$ where Z_2 invariance ν is 1. Negative values of the TRP indicate the partner switching of the Kramers pairs from Λ_1 to Λ_2 , corresponding to a topologically non-trivial band structure. In the second case, the Kramers degeneracy is formed by the same surface states at the different TRIM points resulting in surface state crossing the Fermi level an even number of times (Figure 1.4(c)) and it is possible to drive system into a band insulator by pushing surface states above or below the Fermi level, therefore, corresponding to topologically trivial insulators. TRP for such case is $\pi_a \pi_b = 1$ showing that Kramers pairs do not change the partner across the TRIM points. In conclusion, Z_2 topologically invariant number ν defines the topologically distinct materials by taking 0 or 1 values in 2D system.

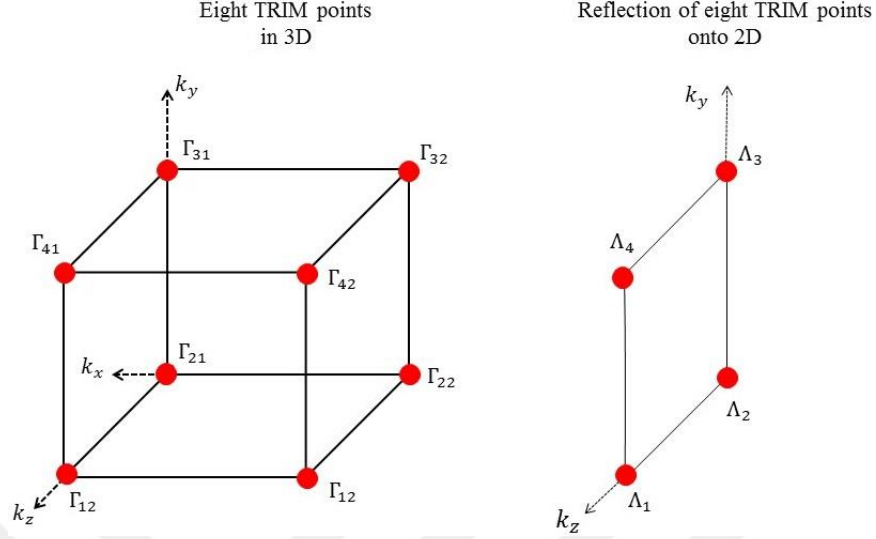


Figure 1.5. Eight TRIM points in 3D and their reflection in 2D as donated by $\Lambda_1, \Lambda_2, \Lambda_3, \Lambda_4$ [14].

Z_2 invariance classification of the QSHI states can be extended to 3D case where “topological insulator” term was first used. Therefore, we prefer to use topological insulator (TI) term instead of the QSHI henceforth. In 3D, there are 8 TRIM points at the corner of the 3D Brillouin zone (Figure 1.5) and Z_2 invariance ν can be written in four components as $(\nu_0; \nu_1 \nu_2 \nu_3)$ for 3D case. Each of the invariance number can take the value of 0 or 1. Similar to the 2D case, ν_0 can be defined as the product of 8 TRIM points [14-15]:

$$(-1)^{\nu_0} \equiv \prod_{n_j=0,1}^8 \delta_{n_1 n_2 n_3} \quad (1.6)$$

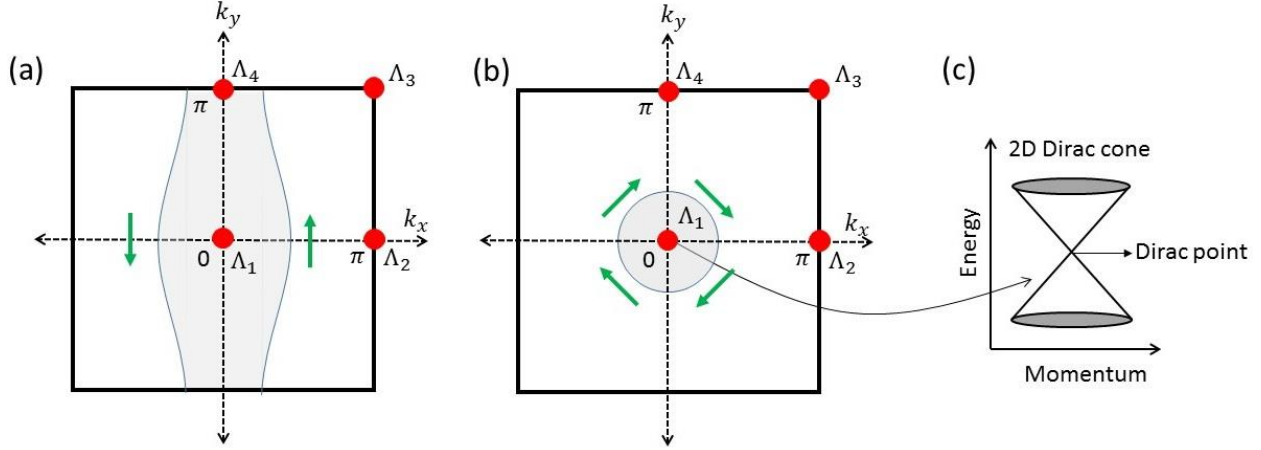


Figure 1.6. Fermi circles represented by shaded areas for a WTI and STI in (a) and (b), respectively. Arrows indicates the electron spin direction. (c) Schematic representation a single Dirac cone enclosed by the Fermi circle in STI system [14].

The rest of the 3 invariants are given by:

$$(-1)^{v_{i=1,2,3}} \equiv \prod_{n_{j \neq i}=0,1; n_i=1} \delta_{n_1 n_2 n_3} \quad (1.7)$$

Similar to the 2D case, δ_i is defined as:

$$\delta_{i=n_1 n_2 n_3} \equiv \frac{Pf[w(\Gamma_\alpha)]}{\sqrt{\det[w(\Gamma_\alpha)]}} = \pm 1 \quad (1.8)$$

Two TRIM points in 3D Brillouin zone can be projected onto one point in 2D square, which are defined by Λ_a (Figure 1.5). TRP associated with the TRIM point Λ_a is given by $\pi_\alpha \equiv \delta_{\alpha 1} \delta_{\alpha 2} = \pm 1$; and the difference between the TRP of the two points defines the topological nature of the band structure. If only two of the eight δ_i have different sign than the other six, topological invariant v_0 is 0. Depending on the other three invariants ($v_1 v_2 v_3$), system can be a band insulator or a weak topological insulator (WTI). If all the three invariants are zero, there is no TRP difference between the any two TRIM points (all have the same parity), corresponding to a band insulator. If

any of the three invariants is different from the other two, there is a TRP difference between the two TRIM points. In this case, surface state encloses even number of the Dirac points making system WTI (Figure 1.6(a)). In WTI, topological surface states can be destroyed by the disorders [14-15]. WTI can be considered as the stacking of 2D TIs since they possess gapless surface states only on the surfaces where the TRP is changed between two TRIM points.

Another class of topological phase can be defined by $\nu_0 = 1$, which is the case where the only one of the eight δ_i has different sign than the other seven. $\nu_0 = 1$ corresponds strong topological insulators (STI). In STI, fermi arc of the surface state encloses odd number of the TRIM points because there is always one TRIM point Λ_a with different sign of the polarization (Figure 1.6(b)). Therefore, TRP changes the sign between the any two TRIM points. In addition, this shows that there must be a surface state crossing the Fermi level in any surfaces of 3D TIs. This type of TIs called STI because surface states cannot be destroyed by disorders due to topological protection by $\nu_0 = 1$ [14-15].

2D and 3D TIs are schematically shown with corresponding band structures in Figure 1.7. 2D and 3D TIs have 1D and 2D Dirac cones, respectively. In both cases electron spin is locked perpendicular to its momentum, which prevents the backscattering of the electrons.

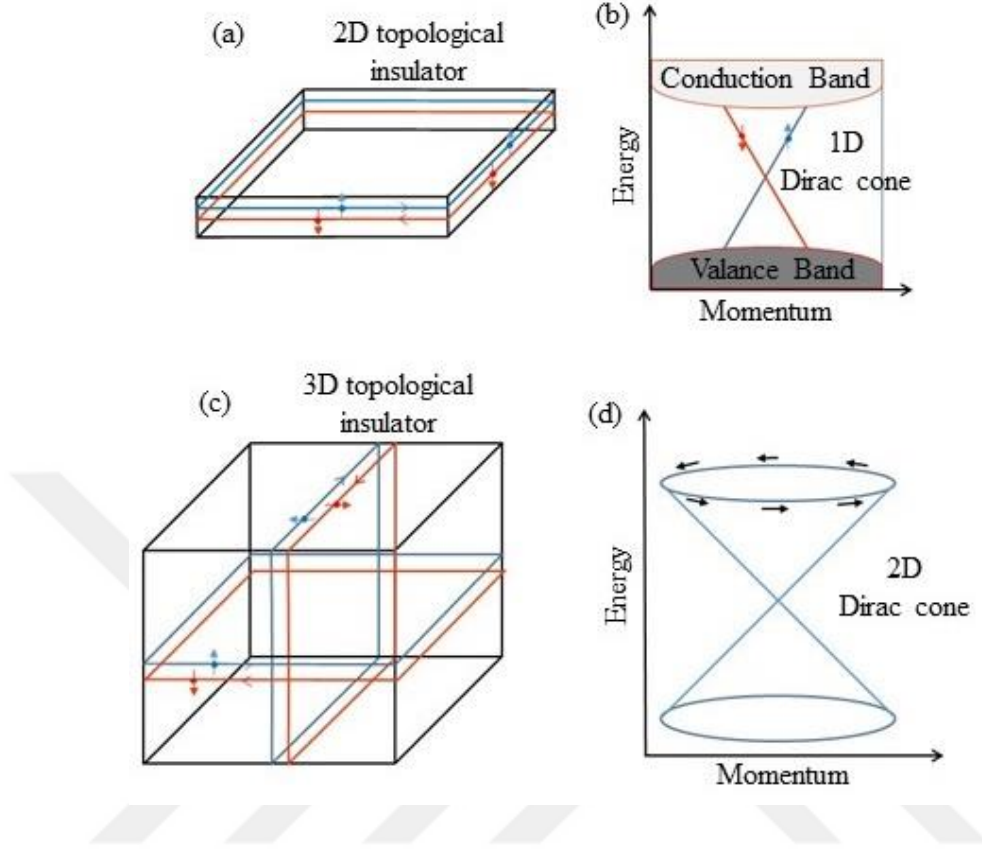


Figure 1.7.(a), (c) Schematic representation of spin filtered conducting edges and surfaces in 2D and 3D TIs, respectively. Different spins propagate in the opposite directions. Spins are represented with arrows. (b) Electronic structure of 1D TI shows 1D Dirac cone. Up and down arrows represent the direction of the spin. (d) 3D Dirac cone on the surfaces of 3D TIs. Black arrows represent to fully spin polarized surface state [17].

Finally, I have introduced the unique surface states and the topological classification of TIs. Regarding the values of the four invariant numbers ($\nu_0; \nu_1 \nu_2 \nu_3$), system can be classified as a band insulator, a WTI, and a STI in 3D system. Among them, STIs are under heavy interest because non-magnetic disorders cannot destroy the surface states in these materials. Topological protection of the surface states makes STIs promising candidates for technological devices. Therefore, it is important to discover these materials experimentally, which is the subject of the next section.

1.4 Experimental realization of 2D topological insulators

Distinct electronic structure of TIs originates from the strong spin-orbit interaction. 2D TI is first theoretically predicted in graphene, which is formed by the single mono-layer of carbon atoms [8]. In contrast to expectations, spin-orbit coupling is extremely weak in this system [11]. This leads scientist to search for a new material with strong spin-orbit coupling; and it was subsequently purposed that HgCd/HgTe/HgCd quantum well (QW) forms the 2D TI above the critical thickness d_c (~ 6.5 nm) of the QW [1,12]. In this system increasing the thickness of the QW leads to the closing and the reopening the bulk band gap by a band inversion between the bulk conduction band and the bulk valance band (Figure 1.8(c), (d)). These inverted bulk bands are connected to each other with a pair of spin filtered edge states, which form 1D Dirac cone at the sample boundaries (Figure 1.8(d)).

2D TI character of HgCd/HgTe/HgCd QW is experimentally confirmed by Konig and his colleagues in 2007 [13]. They performed transport measurement for different thicknesses of the quantum well (QW). Resistance measurements as a function of the applied voltage are shown in Figure 1.8(e) for the sample with the thicknesses of 5.5 nm (Sample I) and 7.3 nm (Sample II, III and IV). The sample I shows a large resistance indicating the band insulator behavior. Increasing the thickness of the QW above the critical thickness of 6.5 nm leads to observe the quantized Hall conductance ($\sigma_{xy} = e^2/h$) under zero magnetic field. In sample III and IV the quantized hall conductance as $2e^2/h$ associated with edge states at the bottom and the top of the samples. Sample III and Sample IV have the same thickness but different lengths, which are $1 \mu m$ and $0.5 \mu m$, respectively. This shows that current is carried only by the sample edges.

So far we introduced the experimental realization of 2D TI in the QW system. In the next section, we continue our discussion by giving the recently performed experiments towards the discovery of 3D TIs.

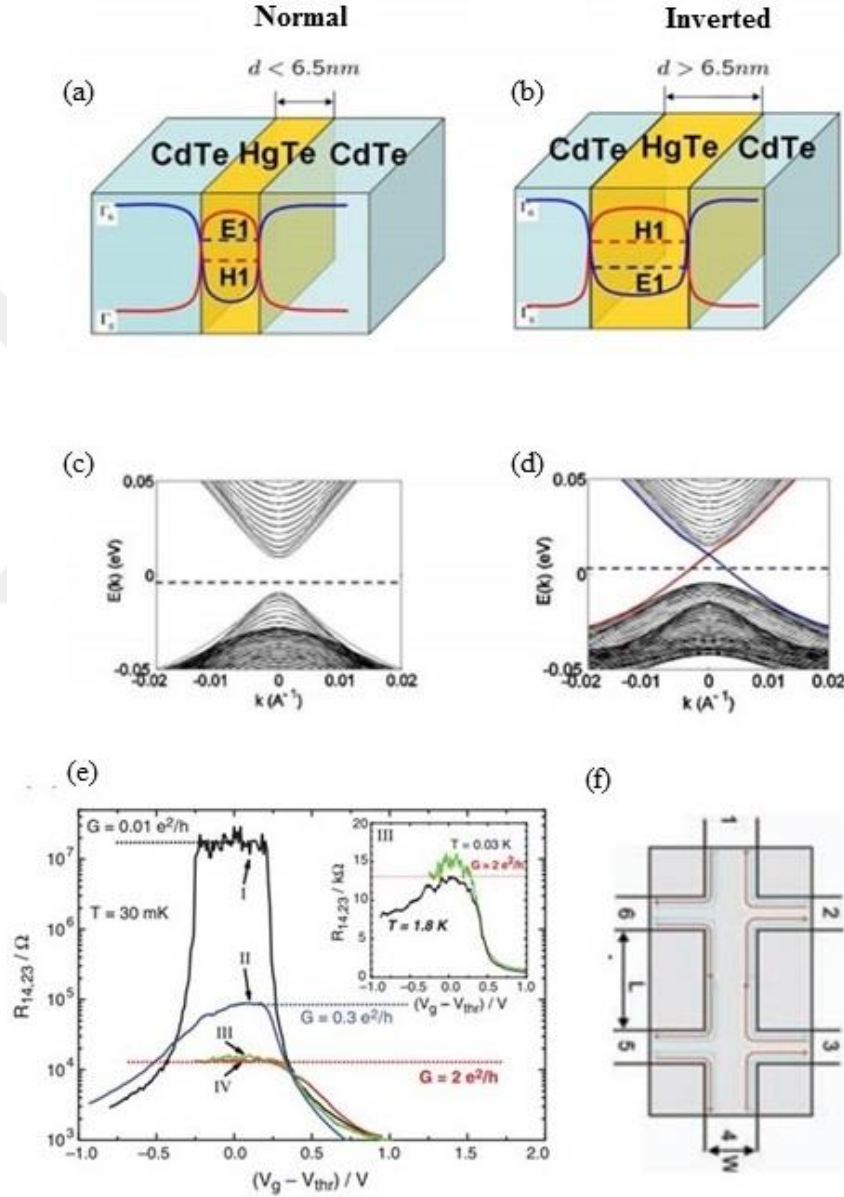


Figure 1.8.(a), (b) Schematic representation of QW below and above the critical QW thickness (6.5 nm), respectively [26]. (c) Electronic structure of normal state. (d) In the inverted region, bulk bands are inverted and topological surface state merges within the inverted bulk band gap [26]. (e) Experimental realization of the QSHI. Inset shows the temperature dependence of Hall resistance [13]. (f) Schematic representation of sample in the transport measurement [13].

1.5 Experimental realization of 3D topological insulators

The experimental realization of 2D TIs pushed experiments to search for 3D TIs. First theoretically predicted and experimentally found 3D TI is Bi-Sb alloy [15-16]. However, this system has highly complicated electronic structure [17]. Second generation of 3D TIs is first theoretically found in Sb_2Te_3 , Bi_2Se_3 , Bi_2Te_3 and experimentally discovered on Bi_2Se_3 , Bi_2Te_3 by angle resolved photoemission spectroscopy (ARPES) [16-20]. These materials are the first real examples of STI. Following the common practice in the literature we employ TI term henceforth instead of STI. 3D TI behavior in these materials are associated with a band inversion of the p-orbitals at the $\Gamma(000)$ point leading to have (1:000) topological invariance numbers. One of the key features of the 3D TIs is to have the Dirac like surface states, which is theoretically and experimentally shown in Bi_2Se_3 and Bi_2Te_3 (Figure 1.9) [18]. ARPES experiment reveal the Dirac like surface states of Bi_2Se_3 and Bi_2Te_3 (Figure 1.9(b) and (e)) [19]. Another important feature of the TIs is helically spin polarized surface states where electron spin is locked perpendicular to its momentum. This can be seen from the spin polarized photoemission experiment performed on Bi_2Te_3 (Figure 1.9(f)) [20]. In plane spin polarization switches the sign from k to $-k$ indicating the existence of spin polarized surface states with helical spin texture.

In summary, I introduced the experimental realization of the unique electron structure of TIs. In the following sections, I will discuss these materials in terms of their importance for experimental realization of the quantum anomalous Hall effect and long sought Majorana fermions, which can be found in magnetic and superconducting TIs, respectively [23-28].

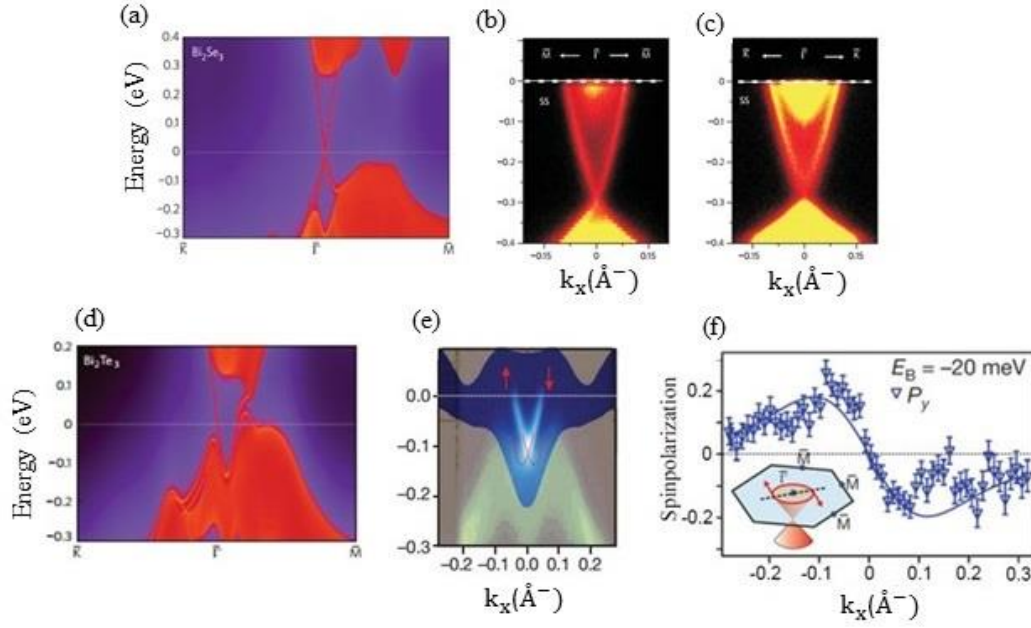


Figure 1.9.(a) Theoretical band structure of Bi_2Se_3 . [18] (b), (c) ARPES electronic structure of Bi_2Se_3 along the different direction in the Brillouin zone. Both spectra show Dirac like surface states [19]. (d) Theoretical band structure of Bi_2Te_3 [18]. (e) ARPES electronic structure of Bi_2Te_3 showing Dirac like dispersion of surface states [20] (f) Spin resolved ARPES measurement performed on Bi_2Te_3 [20].

1.6 Magnetic topological insulators

One of the main interest in this PhD dissertation is the interaction between magnetic impurities and the topological surface states of TIs, which will be investigated in the Chapter 5 and 6 by photoemission spectroscopy technique. The challenges in magnetic TIs is to open a new avenue to possible experimental realization of the quantum anomalous Hall effect (QAHE), which exhibits the characteristics of the QHE in a system without external magnetic field.

Similar to the QHE and ordinary Hall effect, the QAHE is the quantized version of the anomalous Hall effect (AHE). The AHE was first realized by Edwin H. Hall in 1880 after he discovered ordinary Hall effect [29]. He realized that ferromagnetic conductors show larger Hall effect than non-magnetic conductors. The additional contribution to Hall effect is due to the

internal magnetization, which is known as the anomalous Hall effect (AHE). Total Hall effect for ferromagnetic conductor can be expressed by the Hall resistivity (ρ_{xy}) [30]:

$$\rho_{xy} = R_A M + R_H H \quad (1.9)$$

where, the first term in the right side of the equation is the contribution from AHE and the second terms is the ordinary Hall effect contribution with R_H and R_A being the ordinary and the anomalous Hall coefficient, respectively. M and H are the internal magnetization of the sample and the applied magnetic field, respectively. The ρ_{xy} will not go to zero in the anomalous Hall system even if H is zero. This is illustrated in Figure 1.9(a) as magnetic field dependence of the Hall resistance. In the anomalous Hall system, the Hall resistance shows hysteresis loop while it shows linear behavior with respect to magnetic field and passing through zero at the zero magnetic field in the ordinary Hall effect.

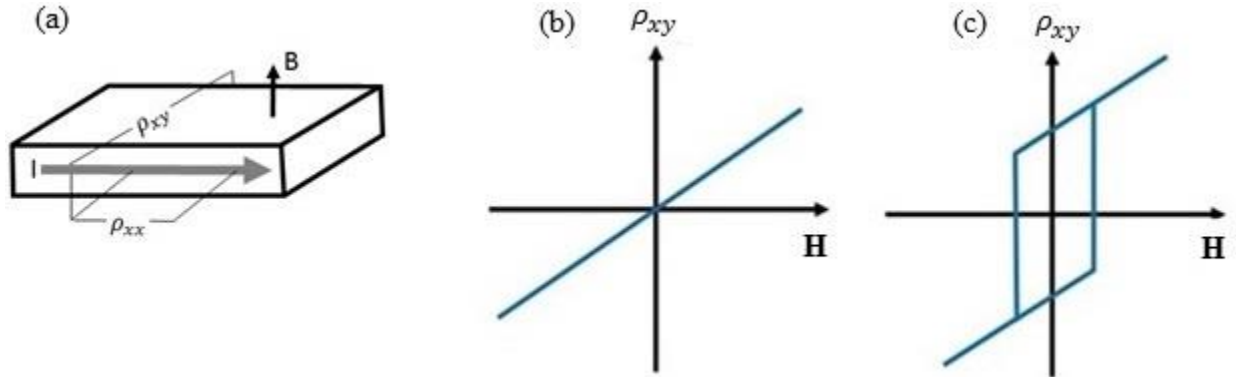


Figure 1.10.(a) Schematic representation of the Hall measurement. (b) Hysteresis loop for ordinary Hall effect. (c) Hysteresis loop for anomalous Hall effect.

As mentioned earlier, Von Klitzing performed similar experiment on Si/SiO₂ field effect transistor, and showed that σ_{xy} quantized form in fundamental units of $\frac{e^2}{h}$, and it is given by:

$$\sigma_{xy} = n \frac{e^2}{h} \quad n = 1, 2, 3, \dots \quad (1.10)$$

It is now inevitable to ask whether there is quantized version of the AHE. First proposal was made by Haldane in 1988 that the QHE can be realized without Landau levels [22]. The model was based on honeycomb graphene lattice under magnetic field with zero net magnetic flux. Graphene possesses the gapless edge states protected by TRS, which can be broken by the magnetic field as in the quantum Hall system. Even though this model suggests the possibility of an experimental observation of the QAHE, it does not predict any realistic material.

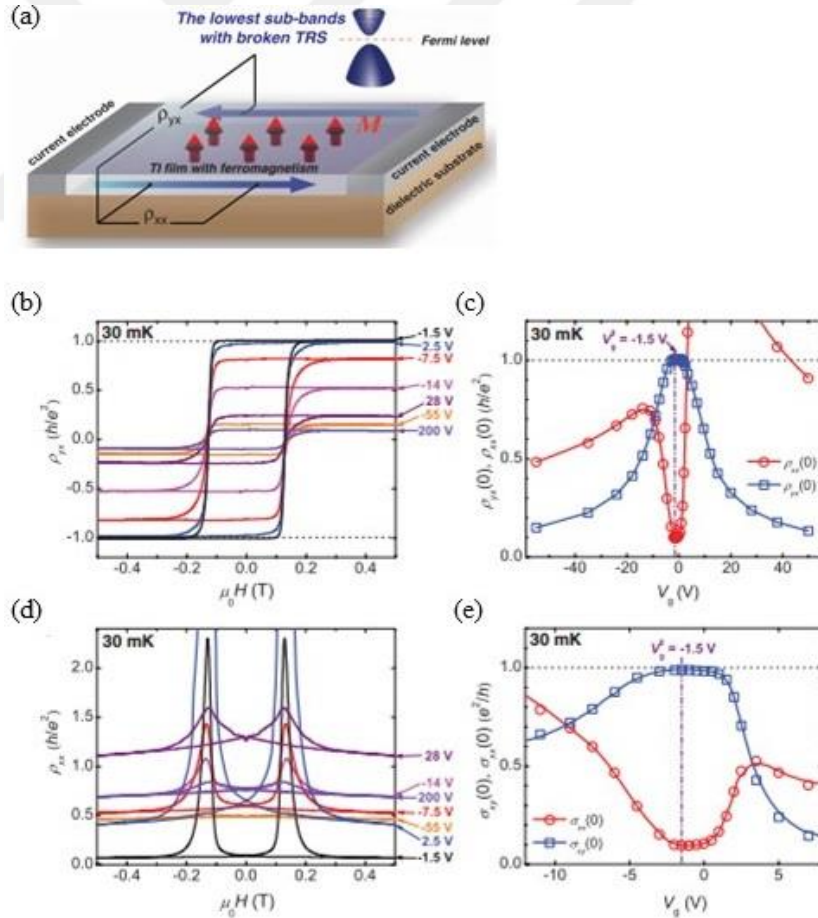


Figure 1.11. The QAHE in 5 QL $\text{Cr}_{0.15}(\text{Bi}_{0.1}\text{Sb}_{0.9})_{1.85}\text{Te}_3$ thin film. **(a)** Schematic representation of experimental geometry. **(b)** Magnetic field dependence of ρ_{yx} at different gate voltages (V_g). **(c)** Gate voltage dependence of $\rho_{yx}(0)$ and $\rho_{xx}(0)$. **(d)** Magnetic field dependence of ρ_{xx} . **(e)** Gate voltage dependence of the Hall conductance $\sigma_{xx}(0)$ and $\sigma_{xy}(0)$ [13].

Recently, the QAHE in magnetically doped TIs was theoretical purposed and experimentally verified [1,13]. The QAHE was observed in Cr doped (Bi,Sb)₂Te₃ TIs, as shown in Figure 1.11 [13]. Magnetic field dependence of ρ_{yx} and ρ_{xx} shows that ρ_{yx} shows a finite value at zero magnetic field while ρ_{xx} falls to zero (Figure 1.11 (b), (d)). In addition, gate voltage dependence of the Hall conductance $\sigma_{xx}(0)$ and $\sigma_{xy}(0)$ at zero magnetic field are given in Figure 1.11 (c) and (d). $\rho_{xx}(0)$ shows sharp drop down to zero at zero gate voltage, while the $\rho_{yx}(0)$ reaches to h/e^2 showing the distinct plateau, which is the characteristic of the QAHE.

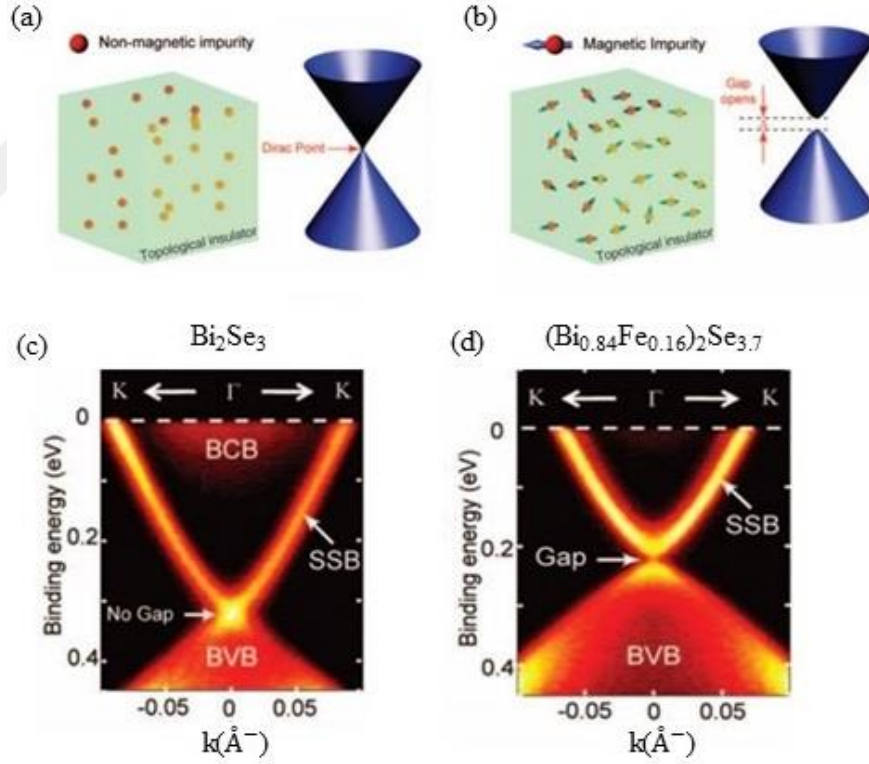


Figure 1.12. (a), (b) Schematic representation of the Dirac cone in pristine sample and magnetically doped sample. (c), (d) ARPES measurements performed on pristine and Fe doped Bi₂Se₃. Pristine sample shows clear Dirac like dispersion, while Fe doping opens an energy gap at the Dirac point [31].

Another consequence of broken TRS is to lift the Kramers degeneracy and open an energy gap at the Dirac point of TIs, which is one of the main interests in this Ph.D dissertation [31]. We gave one of the early study performed on Fe doped Bi_2Se_3 as an example in Figure 1.12. The surface states of Bi_2Se_3 shows Dirac like dispersion (Figure 1.12(c)). Bright feature at the Dirac point indicates the absence of the energy gap. On the other hand, Fe doped Bi_2Se_3 shows the suppressed photoelectron intensity at the Dirac point indicating the gap opening due to broken TRS.

In this section, we presented studies regarding the experimental discovery of the QAHE, and discuss the effects of broken TRS on the electronic structure of TIs. We will continue our discussion by introducing another interesting subject found in TIs; proximity induced superconductivity.

1.7 Majorana fermions in superconducting topological insulators

One of the main experiments done in this thesis is about the superconducting TIs. Superconducting TIs are crucial for providing a promising avenue for experimental observation of long sought Majorana fermions, which are particles theoretically predicted by Ettera Majorana in 1939 [32]. They are described as the zero mode particles, which are their own antiparticles. Current theoretical works suggest that these particles can be observed in the vortex cores of superconducting TIs [25].

In the following sections, I will provide the history and the theory of superconductivity briefly, then continue by presenting recent experiments in the literature towards the observation of Majorana fermions.

1.7.1 Theory of superconductivity

Superconductivity is described as zero electrical resistance and expulsion of magnetic fields (the Meissner effect) of certain materials below the characteristic temperature, which is called the critical superconducting temperature. Superconductivity was first observed by Dutch physicist Heike Kamerling Onnes in 1911 [33]. His observation was made on mercury (Hg) by using the liquid He to cool the specimen for the first time. It was determined that critical superconducting temperature of Hg is 4.1 K. Such experimental observation was first discussed theoretically by Fritz London [34], followed by John Bardeen in 1955 who argued the existence of Meissner effect in superconductors [35]. In 1959, Leon Neil Cooper provided key ingredient to the theory of the superconductivity by calculating bound states of electrons under the attractive force [36]. Finally, BCS theory of superconductivity is developed by John Bardeen, Leon Cooper, John Robert Schrieffer in 1957 [37].

In 1956, Leon Cooper showed that $e^- - e^-$ pair can be formed at adequately low temperature, which has energy lower than the Fermi energy of a superconductor. Lattice distortion takes place due to the attractive force between positive cores and electrons. This attractive force will attract the second electron. If this force is strong enough to overcome repulsive coulomb interaction, there will be net attractive force between two electrons which form the cooper pairs. This lattice distortion is illustrated in Figure 1.13 in the presence of Cooper pair.

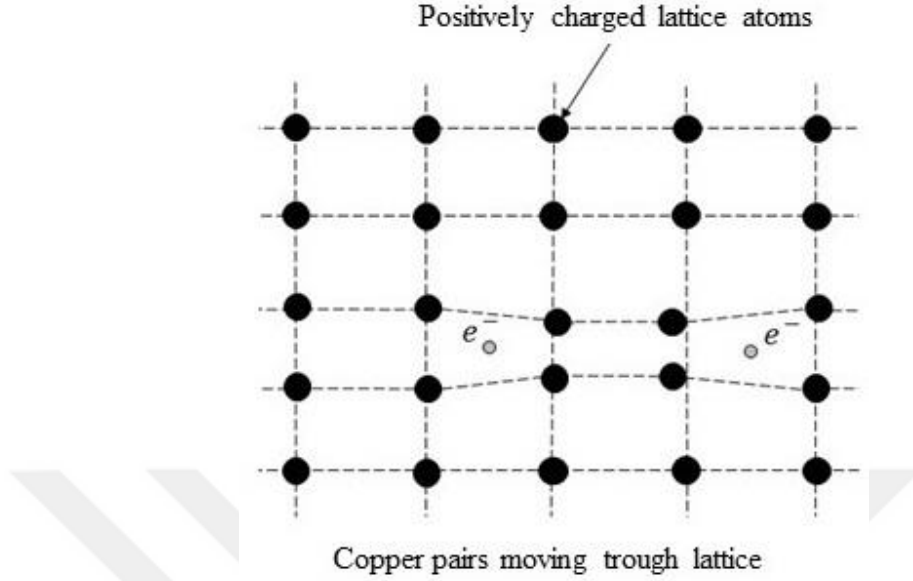


Figure 1.13. Schematic drawing of lattice distortion in superconductors. Black solid spheres represent the positively charged atom cores and gray small balls are the electrons. Two electrons together represent the Cooper pair formed through lattice distortion.

The superconducting gap energy according to by BCS theory is given by [37]:

$$\Delta(T) \cong 3.06k_B T_c \left(1 - \frac{T}{T_c}\right)^{\frac{1}{2}} \quad (1.11)$$

Where, $\Delta(T)$ is the superconducting energy gap at temperature T , k_B is the Boltzmann constant and T_c is the superconducting critical temperature which is related to $\hbar\omega_c$ as [37]:

$$k_B T_c \approx 1.13\hbar\omega_c e^{-\frac{1}{N_0 V}} \quad (1.12)$$

where, N_0 and V are electron density of state at the Fermi level and electron phonon coupling potential respectively, and ω_c is cut-off frequency.

The critical temperature of superconductor can be measured by the transport measurement. In addition, scanning tunneling microscopy and angle resolved photoemission spectroscopy techniques are the wide used tools to measure the superconducting energy gap of superconductors. Furthermore, it is also possible to induce superconductivity on non-superconducting materials,

which is called proximity induced superconductivity [38]. When a non-superconducting material is placed on top of the superconducting one, superconductivity can be induced in non-superconducting material. The emergence of superconductivity is related to penetration of cooper pairs into a non-superconducting material. The proximity induced superconductivity is related to superconducting coherence length introduced by Clark in 1968 after his discovery on superconductivity in the lead-copper-lead sandwiches [38]. The coherence length is given by:

$$\xi_N = \frac{\hbar v_F^N}{T} \quad (1.13)$$

where ξ_N is superconducting coherent length in the normal state, which is described as the penetration length of the cooper pairs into the normal state. v_F^N is Fermi velocity in the normal state. It is important to point out that this length is inversely proportional to temperature, namely lower temperature gives rise to longer penetration depth that can help in the observation of proximity induced superconductivity.

Schematic illustration of superconductor-normal metal heterostructure is given in Figure 1.14. Magnetic field is applied in parallel to observe presence or absence of proximity induced superconductivity by checking the Meissner effect. Since coherence length is important quantity in inducing the proximity effect, the thickness of the normal metal is crucial in such studies.

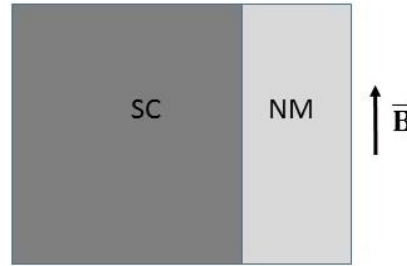


Figure 1.14. Superconducting proximity effect. SC and NM represents the superconductor and normal metal respectively. B is magnetic field applied in plane of the sample to detect proximity effect.

In this section, we introduced briefly the theory of superconductivity. Now, we will provide the recent experimental achievements in the literature to induce superconductivity in TIs and to search for Majorana.

1.7.2 Current experiments towards superconducting TIs and the observation of Majorana fermions

One way of inducing superconductivity in TIs is the bulk doping as achieved in Cu doped Bi_2Se_3 [39]. Transport measurement shows that resistivity drops to zero at 3.8 K showing the superconducting behavior of $\text{Cu}_x\text{Bi}_2\text{Se}_3$ sample with superconducting transition temperature of 3.8 K (Figure 1.15).

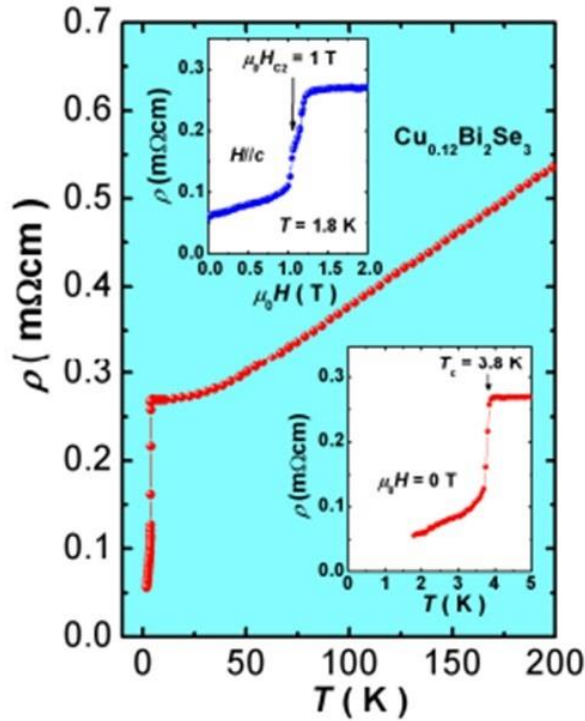


Figure 1.15. Resistivity of $\text{Cu}_{0.12}\text{Bi}_2\text{Se}_3$ as a function of temperature. Lower inset shows the superconducting transition temperature is 3.8 K [39].

As discussed in the theory part, another alternative approach for inducing superconductivity is to use heterostructures, either lateral or layered, involving various superconductors and topological insulators in which the superconductivity would be induced in topological states by a superconducting proximity effect at their interfaces [40–46].

Proximity induced superconductivity is recently observed in 3 quintuple layer Bi_2Se_3 grown on NbSe_2 by S. Y. Xu [47] NbSe_2 is s-wave superconductor with experimentally accessible superconducting transition temperature of 7.2 K. The superconducting coherent length ξ_N of NbSe_2 is about 78 Å [48] making it promising candidate for proximity induced superconductivity in heterostructures. In addition, high crystal quality of Bi_2Se_3 can be grown on NbSe_2 since they have the crystal structure of hexagonal. ARPES measurement taken from 3 quintuple layer Bi_2Se_3 on NbSe_2 at 12 K is presented in Figure 1.16(a). There is an energy gap at the Dirac point due to hybridization between the surface states of sample top and bottom. In Figure 1.16(c) energy dispersive curves (EDCs) were presented at different temperatures. EDCs taken at 12 K and at 7 K do not show any sign of superconductivity because they have the same Fermi level with Au reference. At lower temperature a quasiparticle peak at 1.2 meV is observed and the superconducting energy gap starts to open indicating the merge of superconductivity in Bi_2Se_3 . The quasiparticle peak and the superconducting gap get notable with the lower temperature.

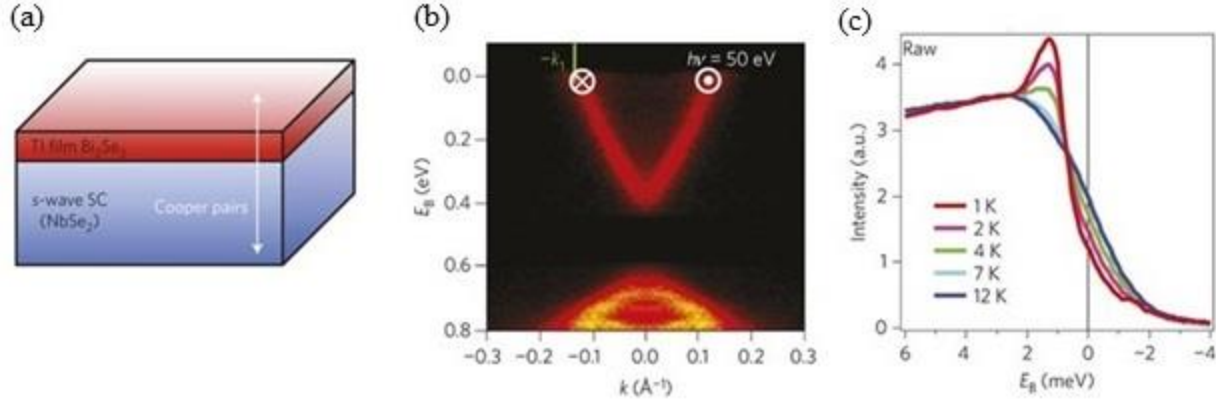


Figure 1.16. (a) A schematic representation of molecular beam epitaxial grown Bi_2Se_3 film on s-wave superconductor NbSe_2 . (b) ARPES 2D intensity of 3 quintuple layer of Bi_2Se_3 grown on NbSe_2 taken with 50 eV photon energy at 12 K. (c) Temperature dependence of energy dispersive curves taken with 50 eV photon energy at $-k_1$ as indicated in (b) [47].

The experiments presented above confirmed the superconductive in TIs. The observation of superconductivity in TIs initiates the discovery of Majorana fermions. Majorana fermions can be found in the superconducting vortex cores. The vortex cores arise from the penetration of the magnetic field into material in the form of quantized flux. The density of state across the superconducting vortex core can be mapped with scanning tunneling microscope (STM) to detect Majorana fermions. One of recent studies is presented in Figure 1.17. Vortex core inside of 5 quintuple layer Bi_2Te_3 grown on NbSe_2 superconductor is shown in Figure 1.17 (b) [49]. In the center of the vortex core a peak appears at zero-bias as shown in Figure 1.17 (c). The peak represents the possible experimental signature of Majorana fermions.

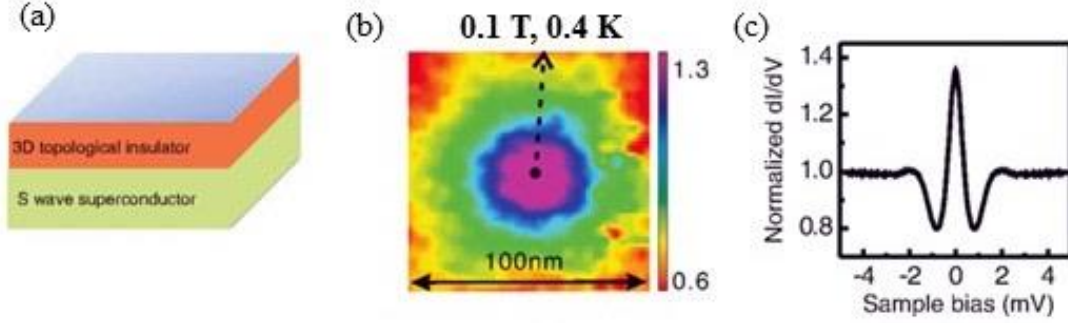


Figure 1.17. (a) A schematic illustration of $\text{Bi}_2\text{Te}_3/\text{NbSe}_2$ heterostructure. (b) Single vortex mapping at zero-bias on 5QL Bi_2Se_3 on NbSe_2 at 0.4 K and 0.1 T. (c) Density of state measurement by STM on the vortex in (b) [49].

Finally, we completed this chapter by giving the recent experiments on the discovery of superconducting TIs, and the experimental signature of Majorana fermions in these systems. We will continue our discussion in the next chapter by introducing the experimental techniques used in this thesis.

1.8 References

1. B. A. Bernevig, and S. C. Zhang, Phys. Rev. Lett. 96, 106802 (2016).
2. E. H. Hall, Am. J. Math. 2, 287 (1879).
3. K. von Klitzing, G. Dorda, and M. Pepper, Phys. Rev. Lett. 45, 494 (1980).
4. R. B. Laughlin, Phys. Rev. B 23, 5632 (1981).
5. B. I. Halperin, Phys. Rev. B 25, 2185 (1982).
6. D. J. Thouless, M. Kohmoto, M. P. Nightingale, and M. den Nijs, Phys. Rev. Lett. 49, 405 (1982).
7. J. E. Avron, R. Seiler, and B. Simon, Phys. Rev. Lett. 51, 51 (1983).
8. C. L. Kane, and E. J. Mele, Phys. Rev. Lett. 95, 226801 (2005).
9. C. L. Kane, and E. J. Mele, Phys. Rev. Lett. 95, 146802 (2005b).
10. M. Z. Hasan, and C. L. Kane, Rev. Mod. Phys. 82, 3045 (2010).
11. Y. Yao, F. Ye, X. L. Qi, S. C. Zhang, and Z. Fang, Phys. Rev. B 75, 041401(R) (2007).
12. B. A. Bernevig, T. A. Hughes, and S. C. Zhang, Science 314, 1757 (2006).
13. M. König, S. Wiedmann, C. Brüne, A. Roth, H. Buhmann, L. W. Molenkamp, X. L. Qi, and S. C. Zhang, Science 318, 766 (2007).
14. L. Fu, C. L. Kane, and E. J. Mele, Phys. Rev. Lett. 98, 106803 (2007).
15. L. Fu, and C. L. Kane, Phys. Rev. B 76, 045302 (2007).
16. D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature (London) 452, 970 (2008).

17. Y. Ando, J. Phys. Soc. Jpn. 82, 102001 (2013).
18. H. Zhang, C. X. Liu, X. L. Qi, X. Dai, Z. Fang, and S. C. Zhang, Nat. Phys. 5, 438 (2009).
19. 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).
20. 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, and M. Z. Hasan, Nature (London) 460, 1101 (2009a).
21. G. Watson, Contemp. Phys. 37, 127–143 (1996).
22. F. D. M. Haldane, Phys. Rev. Lett. 61, 2015 (1988).
23. Y. Tanaka, T. Yokoyama, and N. Nagaosa, Phys. Rev. Lett. 103, 107002 (2009).
24. R. Akhmerov, J. Nilsson, and C. W. J. Beenakker, Phys. Rev. Lett. 102, 216404 (2009).
25. L. Fu and C. L. Kane, Phys. Rev. Lett. 100, 096407 (2008).
26. Qi, X. L., and S. C. Zhang, Phys. Today 63, 33 (2010).
27. C.-Z. Chang et al., Science 340, 167 (2013).
28. Yu, R., W. Zhang, H. J. Zhang, S. C. Zhang, X. Dai, and Z. Fang, Science 329, 61 (2010).
29. Hall, E., Philos. Mag. 12, 157 (1981).
30. H. Weng, R. Yu, X. Hu, X. Dai, and Z. Fang, Adv. Phys. 64, 227 (2015).
31. Y. L. Chen, J.-H. Chu, J. G. Analytis, Z. K. Liu, K. Igarashi, H.-H. Kuo, X. L. Qi, S. K. Mo, R. G. Moore, D. H. Lu, M. Hashimoto, T. Sasagawa, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z. X. Shen: Science 329, 659 (2010).
32. E. Majorana, Nuovo Cimento 5, 171 (1937).
33. Onnes H K, Commun. Phys. Lab. Univ. Leiden 120b 1479–81 (1911).
34. F. London, Phys. Rev. 74, 562 (1948).
35. J. Bardeen, Phys. Rev. 97, 1724 (1955).
36. Leon N., Phys. Rev. 104, 1189 (1956).
37. J. Bardeen, L. N. Cooper, and J. R., Phys. Rev. 108, 1175 (1957).
38. J. Clarke, J. Phys. (Paris), Suppl. 29, C2-3 (1968).
39. Y. S. Hor, A. J. Williams, J. G. Checkelsky, P. Roushan, J. Seo, Q. Xu, H. W. Zandbergen, A. Yazdani, N. P. Ong, and R. J. Cava, Phys. Rev. Lett. 104, 057001 (2010).
40. D. Zhang, J. Wang, A. M. DaSilva, J. S. Lee, H. R. Gutierrez, M. H. W. Chan, J. Jain, and N. Samarth, Phys. Rev. B 84, 165120 (2011).
41. P. Zareapour, A. Hayat, S. Y. F. Zhao, M. Kreshchuk, A. Jain, D. C. Kwok, N. Lee, S.-W. Cheong, Z. Xu, A. Yang et al., Nat. Commun. 3, 1056 (2012).
42. S. Cho, B. Dellabetta, A. Yang, J. Schneeloch, Z. Xu, T. Valla, G. Gu, M. J. Gilbert, and N. Mason, Nat. Commun. 4, 1689 (2013).
43. F. Qu, F. Yang, J. Shen, Y. Ding, J. Chen, Z. Ji, G. Liu, J. Fan, X. Jing, C. Yang et al., Sci. Rep. 2, 339 (2013).
44. M. Veldhorst, M. Snelder, M. Hoek, T. Gang, V. K. Guduru, X. L. Wang, U. Zeitler, W. G. van der Wiel, A. A. Golubov, H. Hilgenkamp et al., Nat. Mater. 11, 417 (2012).
45. J. R. Williams, A. J. Bestwick, P. Gallagher, S. S. Hong, Y. Cui, A. S. Bleich, J. G. Analytis, I. R. Fisher, and D. Goldhaber-Gordon, Phys. Rev. Lett. 109, 056803 (2012).
46. F. Yang, F. Qu, J. Shen, Y. Ding, J. Chen, Z. Ji, G. Liu, J. Fan, C. Yang, L. Fu et al., Phys. Rev. B 86, 134504 (2012).

47. S.-Y. Xu, N. Alidoust, I. Belopolski, A. Richardella, C. Liu, M. Neupane, G. Bian, S.-H. Huang, R. Sankar, C. Fang, B. Dellabetta, W. Dai, Q. Li, M. J. Gilbert, F. Chou, N. Samarth, and M. Zahid Hasan, *Nature Phys.* 10, 943 (2014).
48. S.H. Tessmer, M.B. Tarlie, D.J. Van Harlingen, D.L. Maslov, and P.M. Goldbart, *Phys. Rev. Lett.* 77, 924 (1996).
49. J.-P. Xu, M.-X. Wang, Z. L. Liu, J.-F. Ge, X. Yang, C. Liu, Z. A. Xu, D. Guan, C. L. Gao, D. Qian, Y. Liu, Q.-H. Wang, F.-C. Zhang, Q.-K. Xue, and J.-F. Jia, *Phys. Rev. Lett.* 114, 017001 (2015).



2. Experimental Equipment and Techniques

2.1 Introduction

In this thesis, electronic structure and chemical environment of Bi_2Se_3 and $\text{Bi}_{2-x}\text{Cr}_x\text{Se}_3$ thin films grown by molecular beam epitaxy are studied by photoemission spectroscopy at the surface science laboratory at the University of Connecticut and at the U5 beam line of the National Synchrotron Light Source (NSLS-I) located at the Brookhaven National Laboratory (BNL). In the proceeding sections, schematic description of experimental setups at both places including the film growth facility and photoemission spectroscopy will be introduced. In addition, crystal quality of the thin films was investigated by x-ray diffraction method so the last section will be devoted for the basics of the x-ray diffraction experimental setup.

The uniqueness of the experimental setup used in this work is the vacuum interlocked molecular beam epitaxial growth chamber and photoemission chamber. Such combined system allows performing photoemission experiment on the newly grown samples without contamination under ultra-high vacuum (UHV) condition. We will start with a brief discussion of UHV conditions and UHV chambers before introducing the experimental setups.

2.2 UHV Chambers and Conditions

The essential condition for the molecular beam epitaxial growth and photoemission experiments is UHV condition that is achieved in a stainless-steel chamber. The chamber includes several flanged ports of different sizes, so that the required equipment can be connected, such as a manipulator, viewports and evaporation sources, etc. There are several pressure ranges that can be achieved today, as shown in Table 2.1 and the UHV region covers the pressure between $10^{-8} \text{ torr} > p > 10^{-11} \text{ torr}$.

Table 2.1. Classification of the vacuum regions and the corresponding pressure ranges in torr

Classification	Vacuum Range in Torr
Low	$1 > p > 10^{-3}$
Medium	$1 > p > 10^{-3}$
High	$10^{-3} > p > 10^{-5}$
Very High	$10^{-5} > p > 10^{-8}$
Ultra High	$10^{-8} > p > 10^{-11}$
Extreme Ultra High	$p > 10^{-11}$

Necessity of the UHV condition can be better understood by calculating the formation of a monolayer of air molecules on a sample surface at a given pressure. The impingement rate (number of particles that hit the surface in unite time) for a sticking coefficient of 1 is given by [2]:

$$\Gamma = \frac{p}{\sqrt{2\pi mkT}} \quad (2.1)$$

where p is pressure, m is mass of the particle, k is the Boltzmann constant and T is sample temperature. For example, time required to form a monolayer of air molecules at the room temperature and at pressure of 1×10^{-10} (UHV) torr is up to 8 hours, which is enough time to perform photoemission experiment. Therefore, UHV region is needed so that the experiment can be done on clean surface before the formation of a monolayer of air.

UHV condition is achieved by different pumps connected to the UHV chamber trough the ports. Most commonly used pumps are turbo molecular pump, ion pump and titanium sublimation pump. The details of the UHV chambers and their components is a wide range of knowledge and information. Therefore, we guide readers to Reference 3 for more detailed information.

2.3 Growth Method: Molecular Beam Epitaxy (MBE)

Molecular beam epitaxy (MBE), now widely used in vacuum deposition technology, was developed in the 1970s [1]. The growth method is based on evaporation of high purity source materials onto a substrate surface under UHV condition. Through the interaction between atoms or molecules, desired compounds can form depending on the growth parameters, such as the substrate temperature and the source evaporation rates. In MBE method, source temperatures can be adjusted so that low but stable evaporation rate can be achieved. Therefore, MBE provides unique technique to grow ultra-thin materials with variable stoichiometry and thicknesses down to a monolayer of atom or molecule. This makes MBE the most essential material preparation method nowadays due to recent exotic observations on single monolayer materials. For example, it is found that MBE grown FeSe single monolayer of film has much enhanced superconducting transition temperature of 85 K as compared to the 100 nm film that shows the transition temperature of only 12 K [4]. Another example of novel properties of 2D layers (films) is that of the monolayer of carbon, the well know graphene, which has the spin filtered edge states at the boundary of the 2D sample [5].

A common UHV chamber and its basic components are schematically drawn in Figure 2.1. Evaporators and the Reflection High Energy Electron Diffraction (RHEED) or quartz crystal sensor are attached to the chamber for evaporation and growth rate characterization of the sources, respectively. Vacuum pumps are also connected to a chamber to reach UHV region, and the pressure is read by an ion gauge. Furthermore, one of the most important component of the MBE chamber is the sample holder where samples are loaded for thin film growth. The sample holder is located at the end of the manipulator arm allowing for precise sample position in x , y , z coordinates and θ , φ , ϕ angles. In addition, a leak valve is also occupied for oxide material growth.

Other equipment can be also connected to a MBE chamber depending on the desired experiment such as electron gun for substrate cleaning. Excellent review on MBE growth technique can be found in the literature [1,6-8].

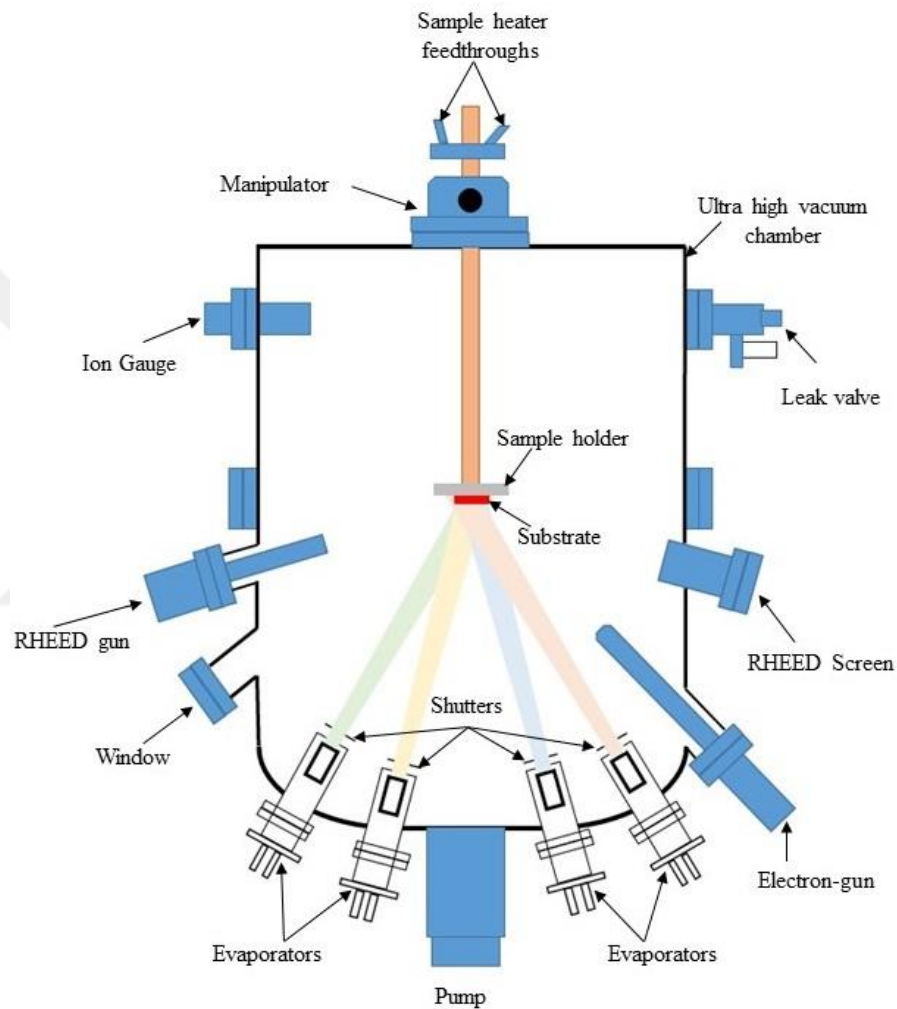


Figure 2.1. Schematic illustration of Molecular Beam Epitaxial (MBE) chamber.

2.4 Components of the experimental setup at the University of Connecticut (UCONN) and at the Brookhaven National Laboratory (BNL)

In this section, experimental setups used in this thesis will be discussed briefly. In order to visualize such systems, schematic drawing of UCONN's MBE-ARPES experimental setup are shown in Figure 2.2. The experimental setup consists of three major parts, the Load-Lock chamber, the MBE growth chamber and the photoemission chamber. Connections between the chambers are through vacuum gate valves, so that the vacuum of each section can be control without effecting the pressure in the other sections. Such combined system provides unique advantage that high crystalline quality thin films grown by MBE can be studied by photoemission technique without surface contamination.

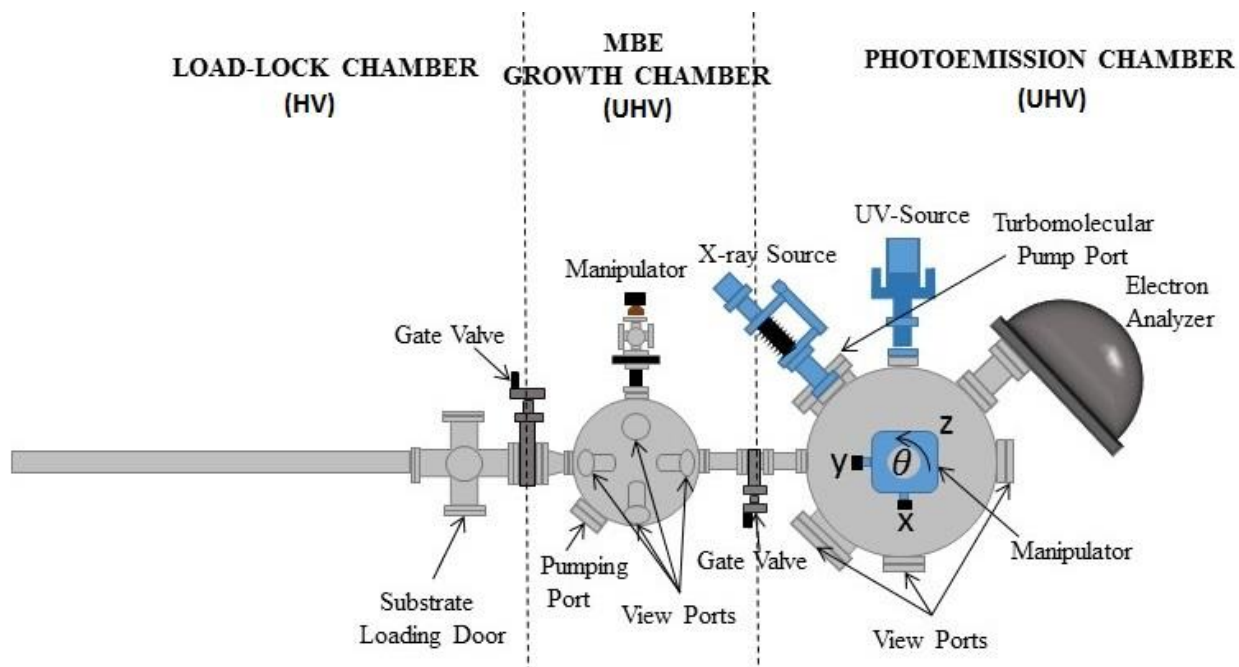


Figure 2.2. Schematic drawing of the top view of experimental setup at University of Connecticut. Evaporators in the MBE chamber are located at the bottom of the chamber (not shown here).

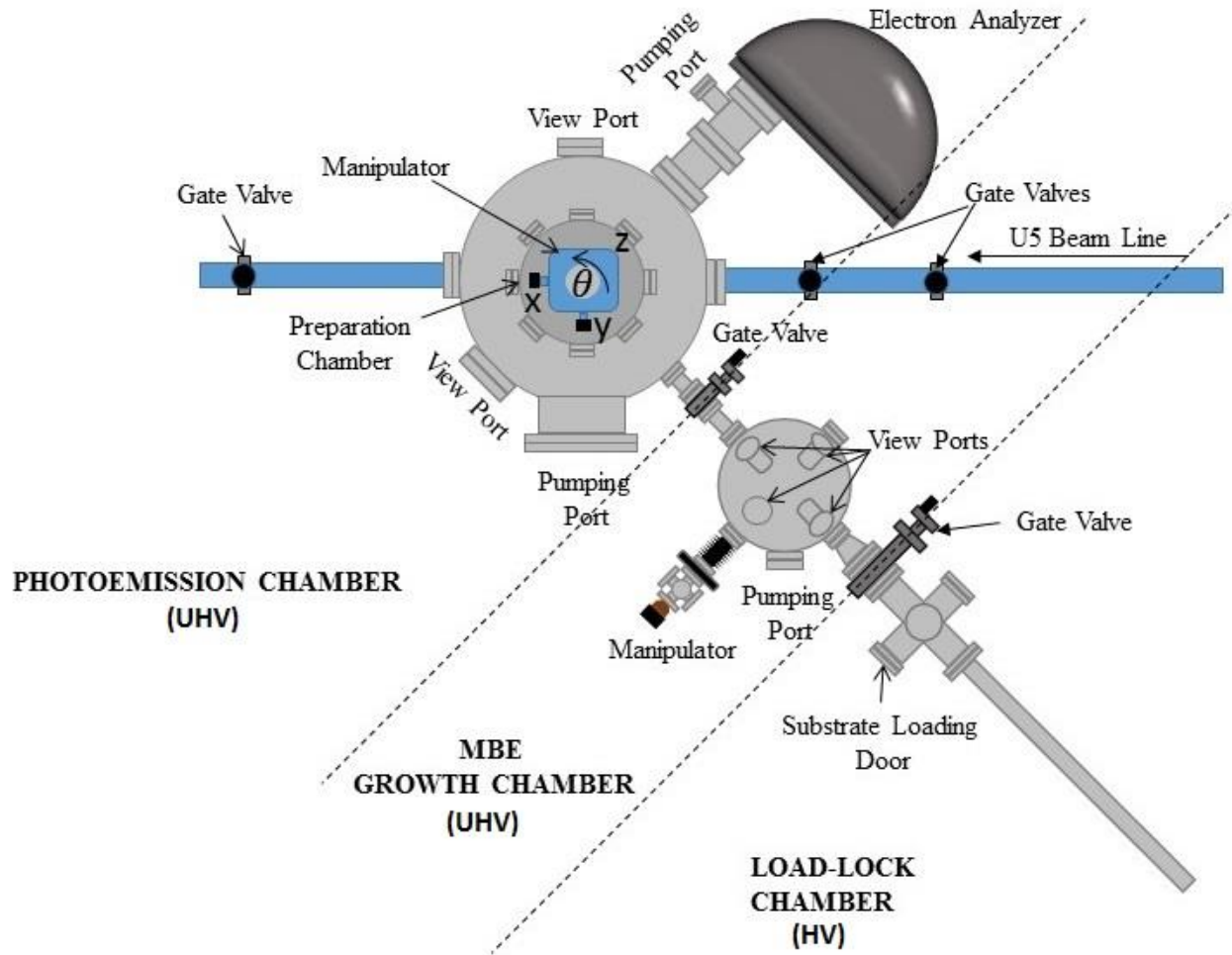


Figure 2.3. Schematic drawing for top view experimental setup at U5 beam line at Brook Haven National Laboratory.

A new substrate is needed to load to MBE chamber for each thin film growth. So, there are two ways to load to substrates, either MBE chamber is vented each time, which consumes a lot of time (for baking the chamber), or we can load the substrates to MBE chamber from another chamber, which operates in high vacuum region. Such chamber is referred to as a LL chamber. First component of the setup is the Load- Lock (LL) chamber that is one of the essential component of such combined systems for sample transfer between the UHV chambers without breaking the

vacuum. The MBE and the photoemission chambers are in the UHV region, which can be achieved by baking the chambers. Such baking procedure usually takes 12 to 24 hours. The main idea of LL chamber is to load crystal substrates in a chamber that can be pumped down to 8×10^{-8} torr in only couple of hours. Since the load-lock is in high vacuum region, it can be opened to MBE chamber to transfer the substrate for film growth, without degrading UHV condition in the MBE chamber.

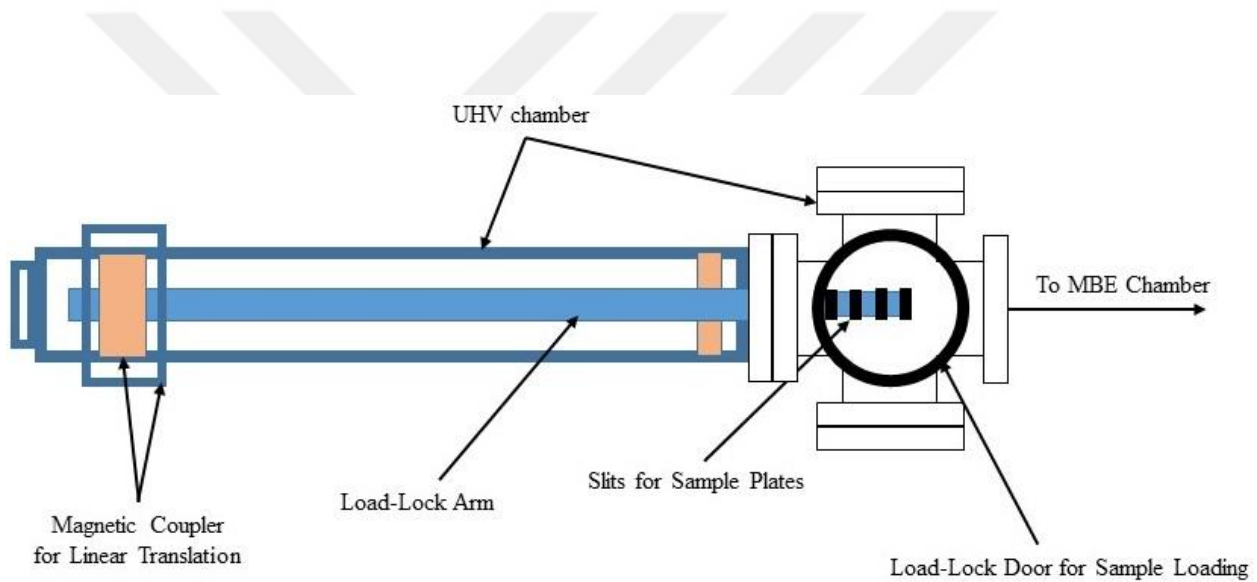


Figure 2.4. Schematic drawing of Load-Lock Chamber.

Schematic representation of a LL chamber is shown in Figure 2.4. It usually includes multiple sample holder and uses transfer the substrates or the films between the chambers without breaking the vacuum. This process usually takes few minutes and vacuum in the MBE chamber and the photoemission chamber can get to its base pressure in an hour.

Another important component of the experimental setup used in this thesis is MBE growth chamber. The schematic drawing of our home build MBE chamber is shown in Figure 2.5. It

consists of three evaporators, a turbomolecular pump, an ion gauge, a quartz crystal sensor, a manipulator, a leak valve (not shown in the figure), a wobble sticks for handling substrate inside the vacuum and view ports.

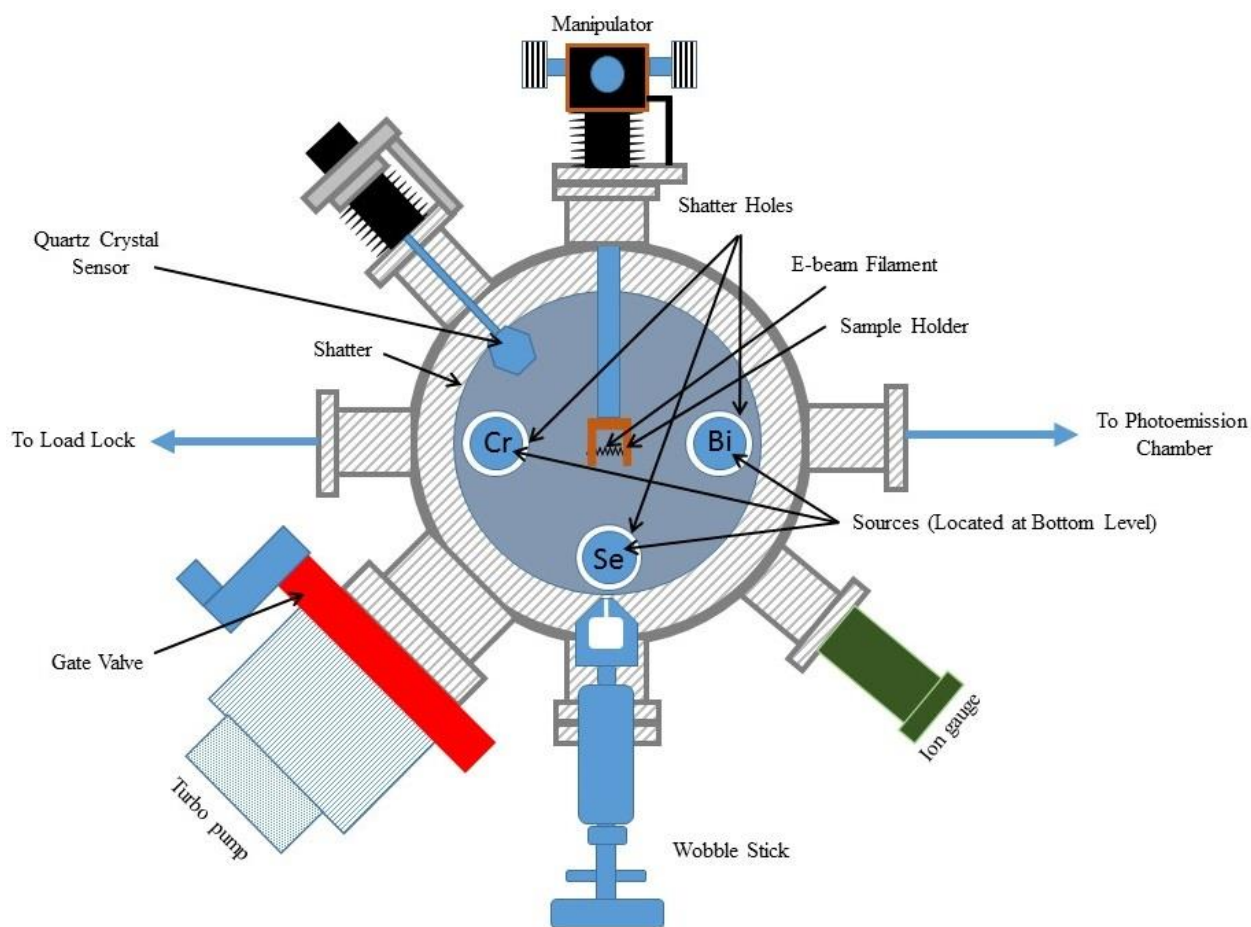


Figure 2.5. Schematic drawing of the top view of the MBE chamber used at UCONN and BNL. Evaporators are located at the bottom of the chamber.

The home-made evaporators used in this thesis are based two different heating methods to evaporate source material, the resistive heating and heating by e-beam bombardment. The evaporators based on these methods are schematically drawn in Figure 2.6.

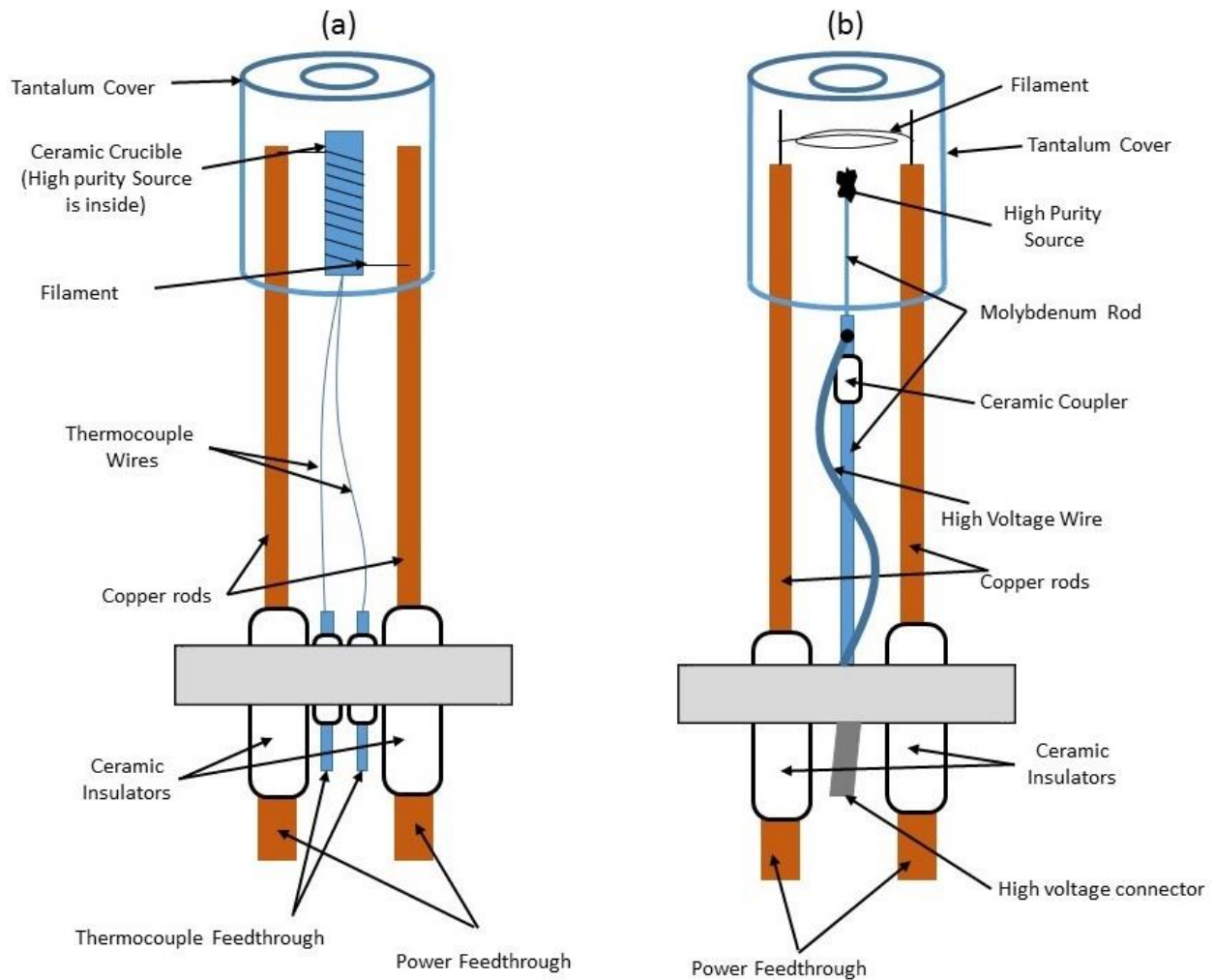


Figure 2.6. Schematic drawing of evaporators used in this thesis. **(a)** Resistive heating evaporator, **(b)** e-beam heating evaporator.

In resistively heating processes, a tungsten wire with a typical diameter between 0.005” to 0.02” is wrapped around the ceramic crucible and ends of the filament are attached to high current Cu electrical feedthrough as seen in Figure 2.6(a). The applied current to the filament results in heating the ceramic crucible and consequently heating the source material located inside the crucible. Temperature of source material is measured with the thermocouple attached to the bottom

of the crucible. In this type of evaporator, it is difficult to heat the source material above 600 °C due to increasing outgassing that comes from the surrounding surface and from the crucible. However, it is good for low temperature evaporation because the source temperature can be controlled simply by current power applied and it is possible to obtain stable low growth rate for ultra-thin film growth.

Second type of the evaporator is based on the electron bombardment. As seen in the Figure 2.6(b), small piece of a source material is attached to the end of the Mo rod, which is electrically isolated from the rest of the evaporator with a ceramic coupler. The source material is connected to high voltage by a HV feedthrough. Electrons thermally ejected from the W filament are accelerated towards the source material under applied high voltage. This results in rapid heating of source material and high temperature of 1000 °C or even higher can be easily reached.

Heating any component inside the UHV chambers cause outgassing, which can degrade the pressure. In order to minimize such effect, number of the components and the surface areas exposed to the heat need to be minimize. Therefore, each evaporator is surrounded by a radiation shield made of Ta foil that prevents heating of the chamber walls and also prevents evaporation of the source material onto other components and chamber walls.

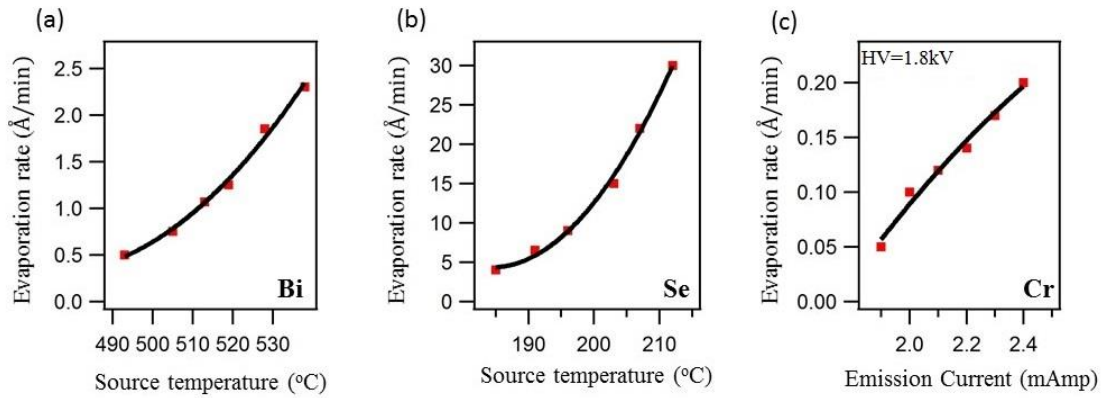


Figure 2.7.(a), (b) Evaporation rates of Bi and Se sources as a function of temperature. (c) Cr evaporation rate as a function of emission current at 1.8 kV high voltage.

In our MBE chamber, resistively heating method is used to evaporate Bi and Se sources, while e-beam evaporation method is applied for Cr evaporation due to its low vapor pressure and high melting point [12]. Evaporation rates of the sources are measured with a quartz crystal sensor and they are shown in Figure 2.7 as a function of source temperature for Bi and Se and as a function of emission current for Cr evaporator.

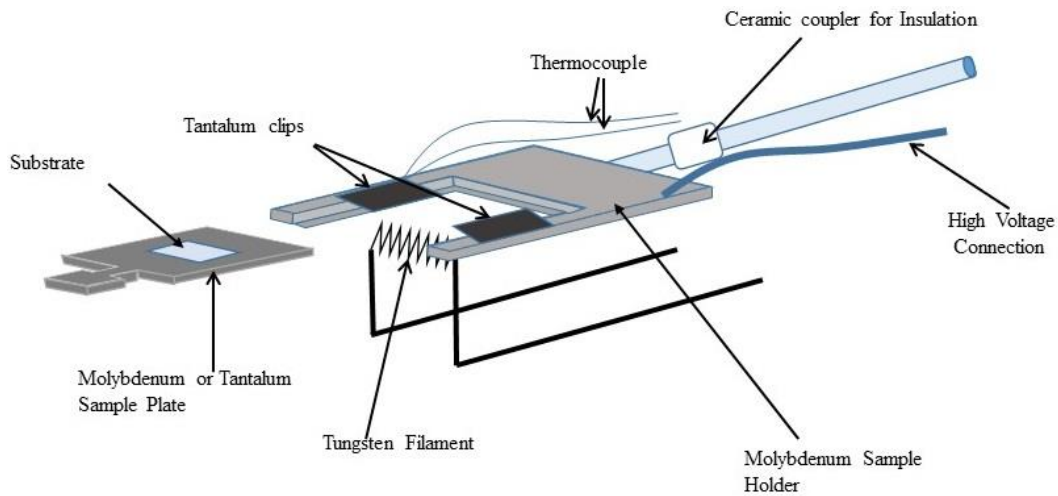


Figure 2.8. Schematic drawing of the sample plate and manipulator sample plate holder. In most of the case, one side of the filament is connected to power supply and other side is grounded.

In MBE method, cleaning of the substrate to obtain atomically flat surface and calibrating the substrate temperature for thin film growth are crucially important to grow high quality of the thin films with right stoichiometry. Therefore, another important component of the MBE chamber is the sample holder where the substrate is loaded and the film growth takes place. Our home-made sample holder and sample plate are schematically shown in Figure 2.8. Substrate temperature is measured through the thermocouple wire attached just next to the sample plate as shown in Figure 2.8. The e-beam method is used in this thesis to heat substrates for cleaning. This method allows for rapid heating of substrates to over 1000 °C. High voltage is applied to substrate and bombardment with electrons thermally ejected from the W filament. Furthermore, Mo or Ta sample plates are used to mount substrate due to their high melting points, which are 2610 °C and 2996 °C, respectively. Importantly, our experience shows that Ta sample plates result in less outgassing making it more favorable to use in experiments that require high temperature annealing.

2.5 Photoemission Chamber

The photoemission chamber used at UCONN is schematically shown in Figure 2.9. It consists of Scienta SES100 electron analyzer, PSP's TX400 x-ray gun for x-ray photoemission spectroscopy, SPECS's UVS20-A UV-lamp for angle resolved photoemission spectroscopy (ARPES). The UV-lamp and the x-ray gun are located at 45° and 0° with respect to center of the lenses of the electron analyzer, respectively. The sample holder has two sides, one for sample heating and another for sample cooling with liquid N₂ or liquid He, which can reach 80 K and 30 K, respectively. UHV condition in the chamber is achieved and maintained by the titanium sublimation pump, the turbomolecular pump and the ion pump.

As mentioned earlier, some part of the experiments presented in this thesis are done at BNL, which has very similar to one at UCONN and it is schematically shown in Figure 2.5. It

consists of more advanced electron analyzer, which is Scienta R4000 electron energy analyzer and photoemission spectroscopy is performed with the synchrotron radiation instead of UV-discharge lamp, which considerable improves the total energy resolution.

In the photoemission experiments, the light source are essential components to generate the photoelectrons and the electron analyzer to record electron intensity at a given energy and the emission angle. In the proceeding few sections, we will briefly introduce these components.

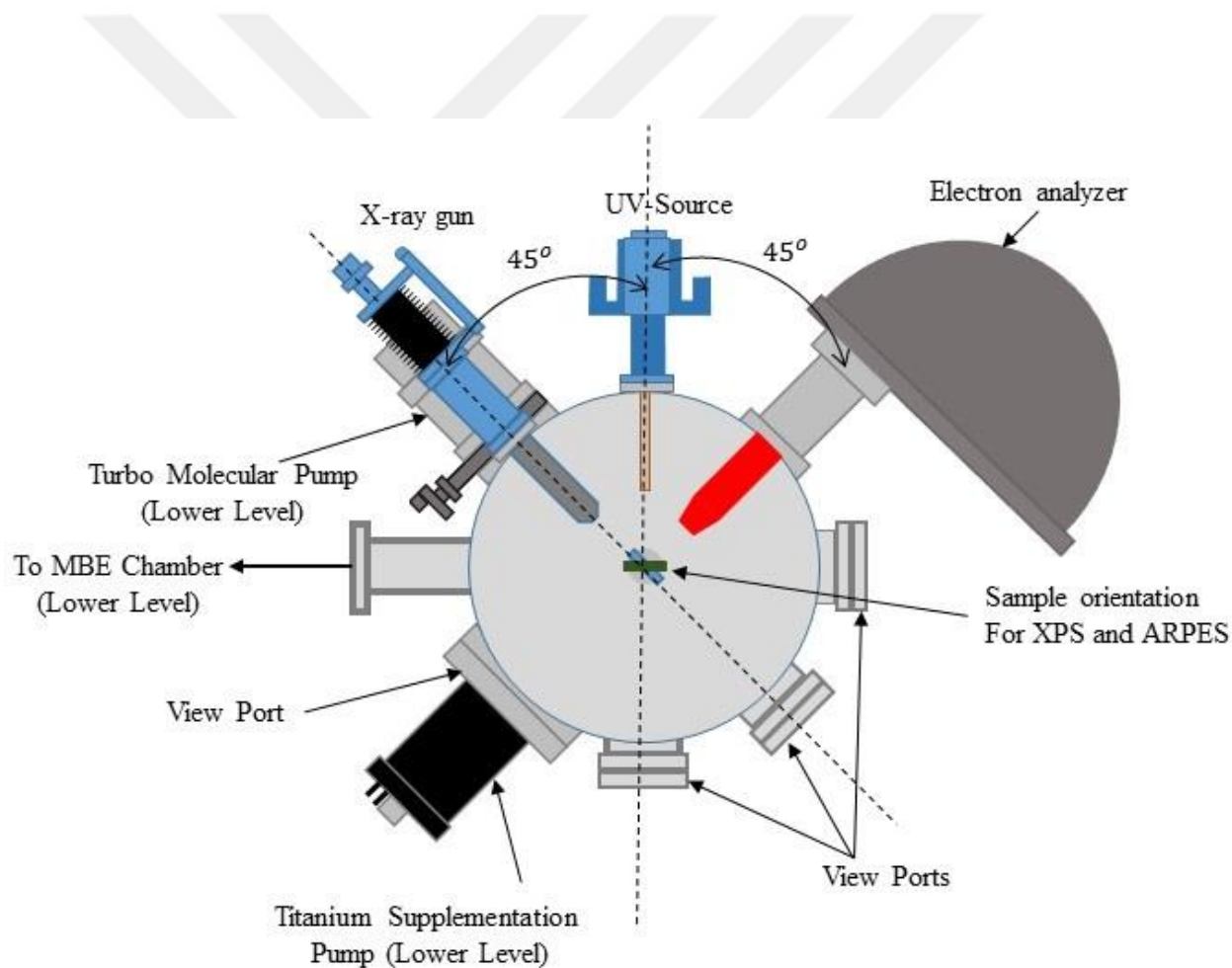


Figure 2.9. Top view of the photoemission chamber at UCONN. Green and blue sample orientation is corresponding to XPS for core-level photoemission spectroscopy and ARPES for electronic structure analyses, respectively. BNL photoemission chamber has similar setup but a synchrotron radiation is used for core-levels and ARPES experiments.

2.6 Photon Sources

2.6.1 X-ray gun

In order to study chemical environment of the thin films, x-ray photoemission spectroscopy is employed at the UCONN's experimental setup. This technique uses the x-ray radiation generated by an x-ray gun. Schematic representation of the x-ray gun is shown in Figure 2.10. It is based on the electron bombardment of the anode elements, which is usually made of Mg or Al. The electrons are thermally ejected from the W filament and accelerated towards anode element, which is under the high voltage. Once high energy electrons hit the target, they can remove the inner shell electrons, if kinetic energy of the impinging electrons is higher than binding energy of inner shell electrons. The electron hole formed in the inner shell can be filled by decay of an outer shell electron. The x-ray radiation will then be emitted with energy determined by the energy difference between outer and inner shell binding energies. Details of this process will be discussed in the next chapter.

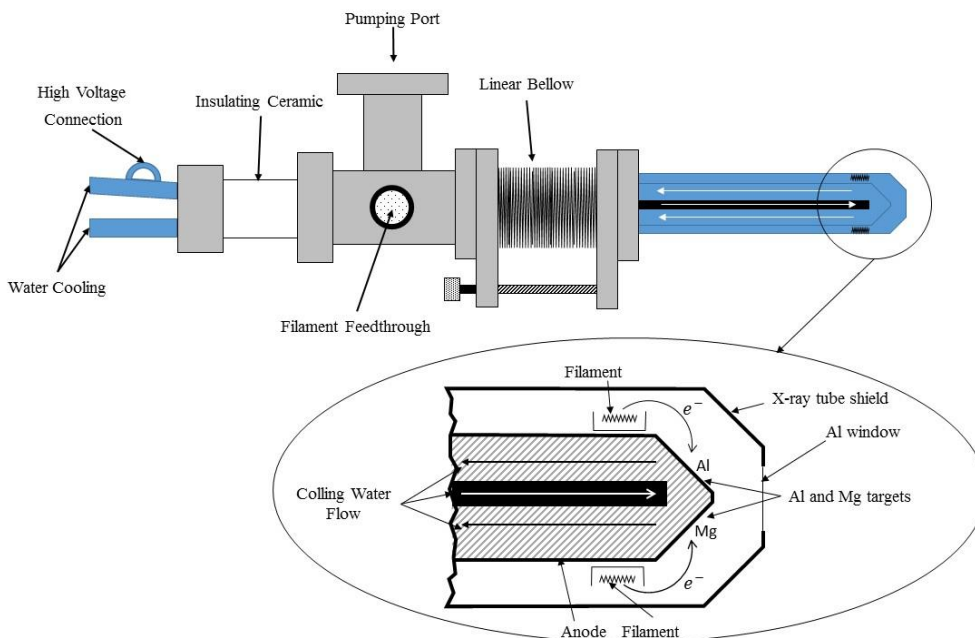


Figure 2.10. Schematic drawing of x-ray gun and close-up view of the head used in core-level spectroscopy at UCONN.

The energy of the x-ray depends on choice of anode material. In our experiment, PSP's TX400 x-ray gun was used to generate Al K_{α} with energy of 1486.6 eV using Al anode. Depending on the required photon energy different anode material can be used to obtain higher or lower photon energy as shown in Table 2.2.

Furthermore, due to high emission current a cooling system is required to keep x-ray gun from overheating as seen in Figure 2.10. Such overheating can result in burning the W filament due to outgassing of heated environment.

Table 2.2. The most common anode elements used in x-ray guns with spectral line and corresponding photon energies

Anode Element	Mg K_{α}	Al K_{α}	Cr K_{α}	Cu K_{α}
Energy (eV)	1253.6	1486.6	5417	8055

2.6.2 UV-Lamp

The most of the work presented in this thesis focuses on the surface electronic structure of the MBE grown thin films. These experiments are usually performed with the radiation in the range of 20 eV to 100 eV. This range of photon energy can produce photoelectrons with the kinetic energies corresponds to the minimum electron mean free path in the solids ($\sim 5\text{\AA}$) making the photoemission experiments highly surface sensitive. In our photoemission experiments, we used SPECS's UVS20-A discharge lamp to generate He I radiation with the energy of 21.2 eV and 3 meV full width at half maximum.

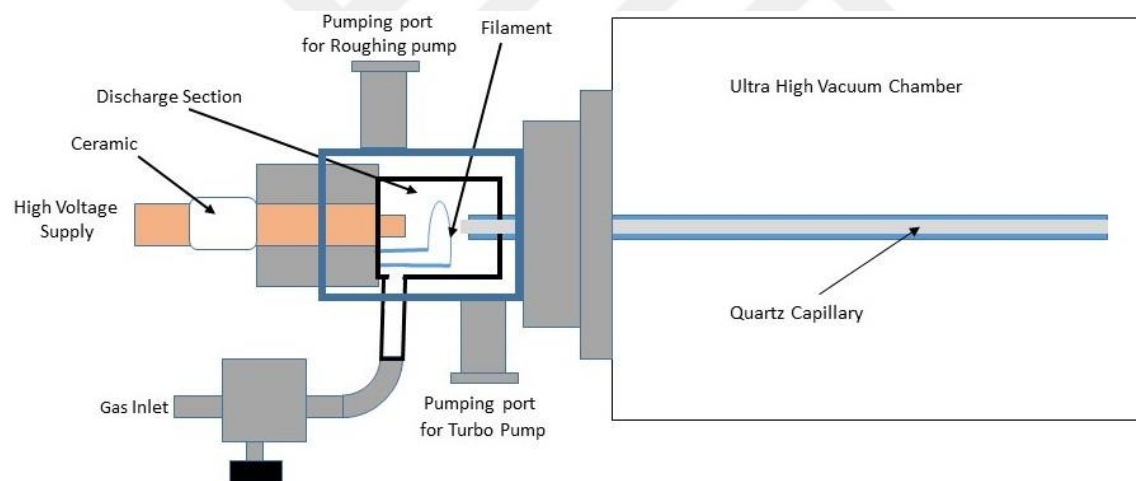


Figure 2.11. Schematic drawing of the UV-lamp. Ultra-high vacuum side is shown with and rectangular. Gas inside the discharge section

The working principle of a UV-lamps is based on the gas discharge, so it is called discharge lamp, and its schematic drawing is shown in Figure 2.11. Gas molecules or atoms in the discharge section collide with electrons ejected from the filament. Such event results in excited gas atoms. Atoms in the excited states return to their ground states by emitting UV radiation. And this

radiation is guided to the sample via quartz tube as seen in Figure 2.11. Except for He, variety of gases can be used, depending on the desired photon energy. List of the gases with corresponding photon energies are given in the Table 2.3.

Table 2.3. Most common gases used in UV discharge lamps with spectral line and corresponding photon energies.

Gas	He I _{α}	He II _{α}	Ne I	Ne II	Ar I	Ar II
Excitation Energy (eV)	21.2	40.82	16.85	26.9	11.83	11.62

2.6.3 Synchrotron Radiation

Due to the limited photon energy range and the low photon flux of the discharge lamps, more advanced light sources are needed for more detailed and complex experiments as presented in this thesis. It is well known concept in physics that electrons accelerating under magnetic field emit radiation, which is known as the synchrotron radiation. Such radiation is used in variety of spectroscopic techniques at many synchrotron facilities around the world. Electrons are confined to move inside the storage ring, which contains different experimental stations for different type of experiments. Several advantages of such facilities include high photon flux with narrow line width and wide range of photon energy from ultraviolet to hard x-ray.

Basic components of the synchrotron radiation facilities are shown in the Figure 2.12. In the first stage, the accelerated electrons enter the ring, which is essentially UHV chamber in the shape of circular tube. Radio frequency cavity is responsible for supplying energy to the electrons moving in the ring. Such electron beam will circulate inside the ring due to presence of bending magnets. Bending magnets help the electron beam keep its circular motion, and it also leads to

electrons emitting synchrotron radiation. Other devices inserted into the storage ring system are wigglers and undulators. Wiggler consists of few period of magnets, while undulators consists of many period of magnets attached in alternative direction along a straight port of the storage ring. These are devices composed of periodic array of magnets. Once the electron beam enters into such an array of magnets, it will undulate (wiggle), therefore it will emit the light. Advantage of such array of magnets is to produce more intense radiation compared the bending magnets. The wiggler emits high brightness broad spectra in electromagnetic spectrum while the radiation emitted from an undulator is even more intense and collimated in narrower energy range.

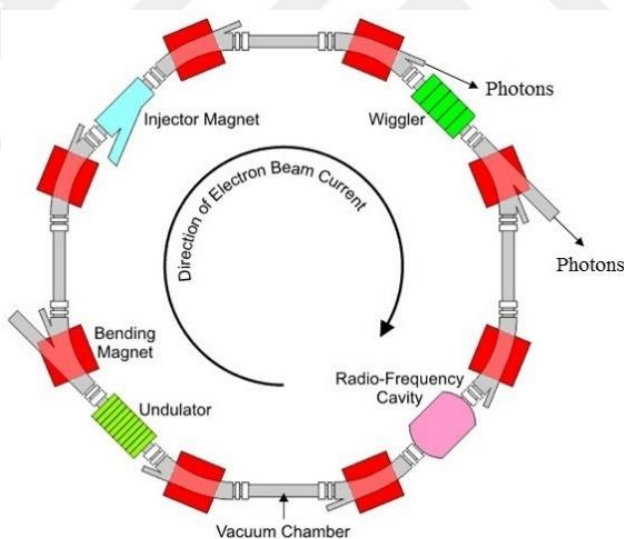


Figure 2.12. Technical representation of the synchrotron radiation facilities. According to the purposes, different experimental stations are setup at the end of each beam line, such as, ARPES station [10].

2.7 Hemispherical Electron Analyzer

The electron analyzer is the main instrumentation component for performing the photoemission spectroscopy. It is used to measure electron intensity versus photoelectron

momentum and energy. The analyzers consist of the three main parts, the electron lens, the energy analyzer and the electron detector (multi-channel electron plate). The most common electron analyzer used today is hemispherical electron analyzer. Its schematic representation is shown in Figure 2.13.

The electrons ejected from the sample will travel straight to lens in the field free region. The purpose of the electron lens is to focus the electrons onto entrance slit of the analyzer. The analyzer separates electrons according to their initial kinetic energies and detector records the data as photoemission spectra.

As seen in Figure 2.13, the electron analyzer consists of two hemispherical electrodes with radius r_1 and r_2 . Electrons are guided in different orbits by the voltage difference between the hemispheres. The electrons that travel through the hemispheres with a radius r_0 will pass through exit slits of the analyzer and will be detected. Kinetic energy of the electrons is retarded to a constant kinetic energy called E_p (Pass Energy) by the electrostatic lenses before entering the analyzer. The pass energy of the hemispherical electron analyzer is given by:

$$E_p = q \left(\frac{r_1 r_2}{2r_0(r_2 - r_1)} \right) \quad (2.2)$$

where q is electron charge and ΔV is the voltage difference between outer and inner hemisphere and it is given by $V_1 - V_2$, r_0 is $(r_2 + r_1)/2$. Kinetic energy of the electrons entering the hemispheres will be retarded or accelerated by the voltage of V_0 . Therefore, measured kinetic energy of the electron is given by,

$$E_K = E_p + qV_0 \quad (2.3)$$

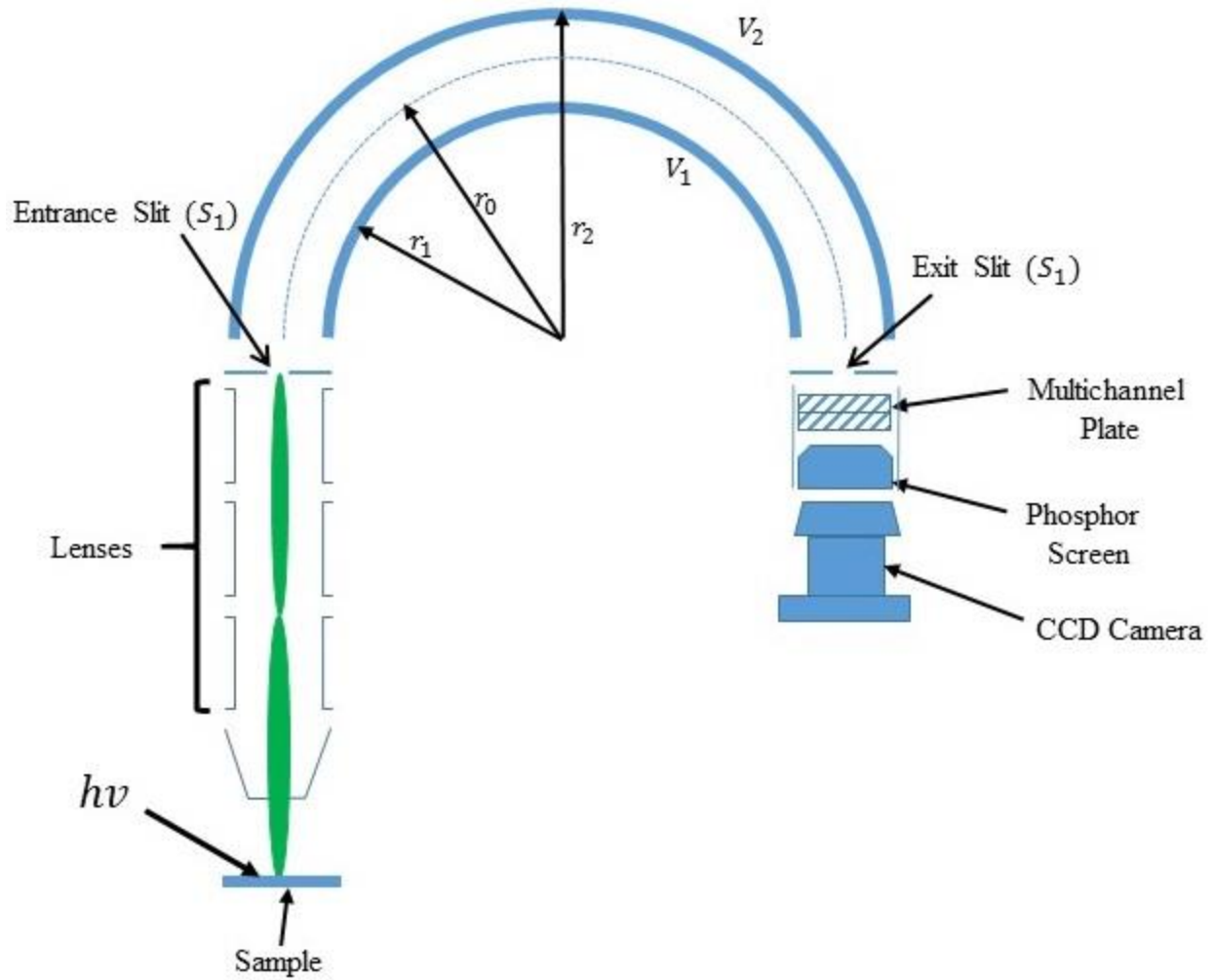


Figure 2.13. Schematic drawing of the hemispherical electron analyzer.

Furthermore, the energy resolution of the hemispherical electron analyzer is defined as,

$$\Delta E = E_p \left(\frac{S}{2r_0} + \frac{\alpha}{4} \right) \quad (2.4)$$

where α is the acceptance angle of the lens and S is the average of entrance and exit slits widths ($S = (S_1 + S_2)/2$) in the energy dispersive direction. From this equation, the energy resolution of the electron analyzer can be improved by building analyzer with larger r_0 , or smaller

slit width. However, smaller slit width leads to lower the photoelectron intensity. Thus, it is convenient to use more intense photon source in order to enhance the energy resolution in the electron analyzer without losing the photoelectron intensity. That is one of the reason making synchrotron facilities so attractive. Because, they have higher photon fluxes than the laboratory sources synchrotron radiation generates high photoelectron intensity. It is than possible to reduce the slit width in order to increase the energy resolution, while having sufficient photoelectron intensity.

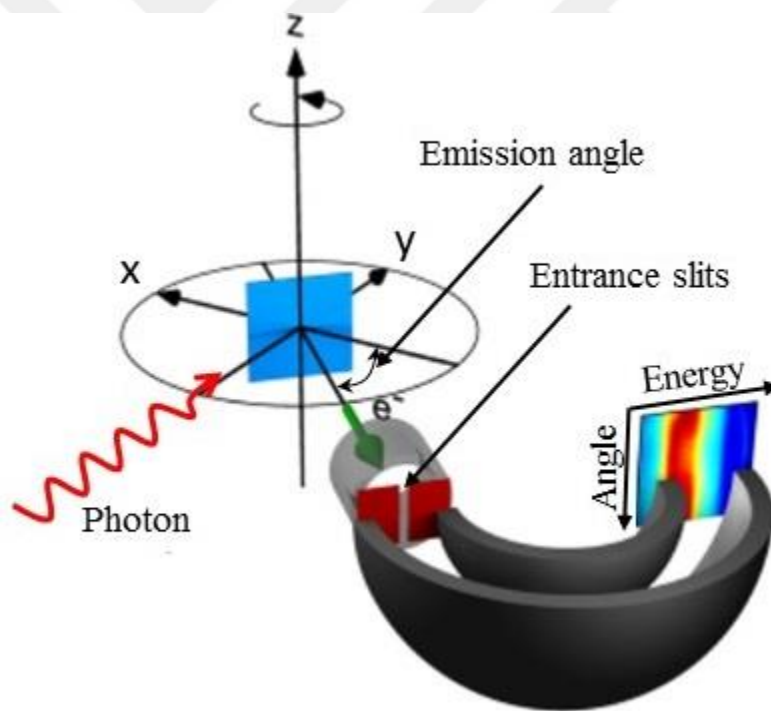


Figure 2.14. 3D view of modern electron analyzer

Once the electrons pass the hemispherical analyzer they reach a detector. Modern electron analyzers as used in this thesis employ 2D electron detector allowing to record simultaneously dispersive curves at wide range of the energy and the angle of the photoemitted electrons. The

position electron hits on the 2D detector determines the kinetic energy and the emission angle of the photoelectron. When the number of photoelectrons emitted at different emission angle are considered, the resulting data is 3D matrix consisting of the photoelectron intensity versus the kinetic energy and the emission angle of the photoelectron. Such advanced 2D electron detector opens easy way for the Fermi surface mapping by recording the spectra at different emission angles. For such experiment, sample orientation with respect to slits in the electron analyzer is schematically shown in Figure 2.14. In order to perform such experiment, electron analyzer has to be placed in such a way the slits in the electron analyzer is along the z-axis as indicated in Figure 2.14. The sample has to be rotated so that photoelectron intensity as a function of energy and angle can be measured along the other directions (y-axis).

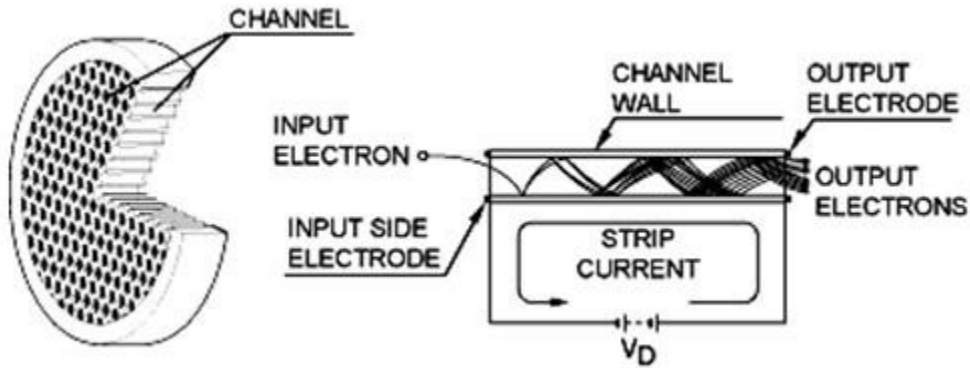


Figure 2.15. Drawing of MCP detector and single channel [11].

Advanced detectors are multi-channel plates (MCP), which consists of many channels that multiply number of electrons and consequently this increases the measured photoelectron intensity. After electrons pass through MCP, they are further accelerated and hit the phosphor screen, which generate visible light flashes, which are recorded by the CCD camera. The

photoemission spectrum is formed by recording the photoelectron signal from CCD camera as a function of scanning voltage V_0 . Finally, the captured image by the CCD camera is represented photoelectron intensity versus the energy and the angle.

2.8 X-ray diffractometer

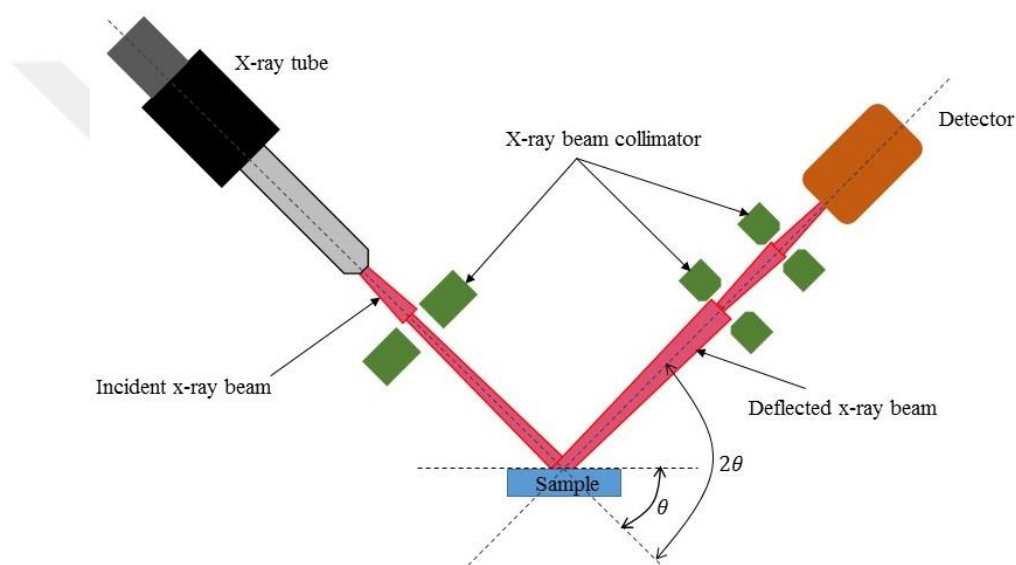


Figure 2.16. Schematic drawing of x-ray diffractometer.

In order to determine lattice constants and crystal structure Bruker D2 Phaser x-ray diffractometer was used in this thesis. X-ray diffractometer is common tool for structural analysis and it measures the x-ray beam scattered from the sample. Simple x-ray diffractometer consists of the x-ray tube, the detector and the x-ray beam collimator as shown in Figure 2.16. The x-ray beam collimator is used for precisely define the x-ray beam direction onto sample. It consists of lead shatters that completely absorbs the unwanted x-ray beams. The detector measures the flux and spatial distribution of reflected x-ray beam.

Depending on the type of experiments, XRD data can be collected under two experimental configurations. One is that x-ray source remains fixed, while sample and detector rotate θ and 2θ , respectively. Another way to collect XRD data is by x-ray source and detector rotating by θ clockwise and anticlockwise, respectively, while sample is in fixed position. In our work, the sample is fixed, while the x-ray source and the detector rotate in a range of angle and the detector records the flux intensity of x-ray and 2θ . We use x-ray source Cu K_{α} with wavelength of 0.154184 nm in our work.

2.9 References

1. A. Y. Cho and J. Arthur. Molecular beam epitaxy. Progress in Solid State Chemistry, 10:157–191 (1975).
2. R. A. John, Surface Science 500, 189–217 (2002).
3. H. H. Marsbed, High-Vacuum Technology: A practical Guide, Marcel Dekker Inc. 2th edition, (1997).
4. S. Y. Tan, M. Xia, Y. Zhang, Z. R. Ye, F. Chen, X. Xie, R. Peng, D. F. Xu, Q. Fan, H. C. Xu, J. Juan, T. Zhang, X. C. Lai, T. Xiang, J. P. Hu, B. P. Xie, and D. L. Feng, Nat. Mater. 12, 634 (2013).
5. P. W. Sutter, J. I. Flege, and E. A. Sutter, Nature Materials, Vol.7, p. 406 (2008).
6. J. R. Arthur, Surf. Sci., 500, 189 (2002).
7. M. B. Panish, Science 208, 916 (1980).
8. R. A. John, Surface Science 500, 189–217 (2002)
9. J. T. Yates, Jr. Experimental Innovations in Surface Science, Springer, 1st edition, (2011)
10. <http://pd.chem.ucl.ac.uk/pdnn/inst2/work.htm>
11. http://www.dmphotronics.com/MCP_MCPIImageIntensifiers/microchannel_plates.htm
12. http://www.vem-co.com/sites/default/files/pdfs/VEM_Thin_Film_Evaporation_Guide.pdf

3. Theories of Experimental Techniques

3.1 Introduction

In the previous section, we introduced the experimental equipment and setups at the University of Connecticut (UCONN) and at the U5 beam line of the National Synchrotron Light Source (NSLS-I) located at the Brookhaven National Laboratory (BNL). In this chapter, the physics behind these techniques will be introduced. Most of the work presented in this thesis are the photoemission studies of the Molecular Beam Epitaxial (MBE) grown thin films. Therefore, we will start by giving physical principle of the generation of x-ray, ultraviolet (UV) and synchrotron radiation, which are used as radiation sources to generate photoelectrons in the photoemission experiments. Then we discuss the photoemission process in X-ray Photoemission Spectroscopy (XPS) and Angle Resolved Photoemission Spectroscopy (ARPES). The last section is devoted for the theory of X-Ray Diffraction (XRD), which is used for crystal structure analysis in this work.

3.2 Principles of Generating X-ray, UV and Synchrotron Radiation

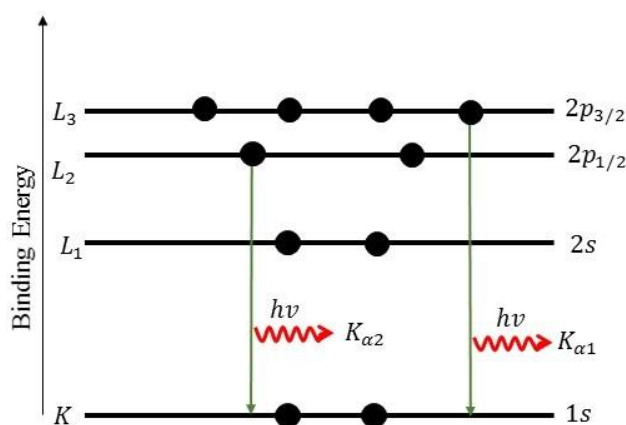


Figure 3.1. Schematic representation of x-ray radiation generation.

One of the common light source used in photoemission spectroscopies is the x-ray radiation, which can be produced by simple x-ray gun as shown in the previous chapter. Generation of the x-ray radiation is schematically shown in Figure 3.1 by the electron energy levels picture. In this example, electron hole is formed in the $1s$ energy level (K-shell) by high energy electron bombardment. This core hole-state can be filled by an electron found in the upper energy levels. However, such transition from upper to the lower energy level can only happen when the dipole selection rule is satisfied, which require the change of the angular momentum (L) such that: $\Delta L = \pm 1$. Therefore, electron hole in the $1s$ can be filled by the electrons from the $2p$ orbital, since s and p orbitals have 0 and 1 angular momentums, respectively. Once the electron from the $2p$ orbital fills the $1s$ hole, $K_{\alpha 1}$ and $K_{\alpha 2}$ x-ray radiations are emitted as shown in Figure 3.1. The reason of having two different transition is due to spin-orbit splitting of the p orbital into the two energy levels: $p_{1/2}$ and $p_{3/2}$ resulting in two different transitions. Energy of the x- ray radiation is precisely equal to the difference between the final and the initial states of the electron, and it can be calculated as:

$$E_{hv}(K_{\alpha 1}) = E(1s) - E(2p_{3/2}) \quad (3.1a)$$

$$E_{hv}(K_{\alpha 2}) = E(1s) - E(2p_{1/2}) \quad (3.1b)$$

where $E(1s)$ and $E(2p_{3/2})$ represent the inner electron shell binding energies. For the Al-metal target, which is used in this thesis, $K_{\alpha 2}$ and $K_{\alpha 1}$ photon energies are 1486.27 eV and 1486.7 eV, correspondingly [21]. Due to life time broadening the two lines are not resolved but form single a x-ray line with a width of ~ 0.85 eV.

Another source used in this work is He-I radiation, which can be generated in UV-discharge lamp. This kind of radiation is produced as a result of the collision between the electrons and the

gas atoms. The collision leads to excitation of the $1s$ electron to the $2p_{3/2}$ energy level in He atom. When the atom returns to its ground state, the He-I radiation is emitted with the energy of 21.22 eV, which corresponds to the energy difference between the initial and the final state of the electron as in x-ray radiation generation. This process can also produce the He-II radiation, which is the emitted radiation from the single ionized He atoms, and its photon energy is 40.18 eV.

In photoemission experiment, sampling depth is restricted by the mean free path of the photoelectron, which depends on the kinetic energy. The photoelectrons within the kinetic energy range of 20 eV to 50 eV have the lowest electron mean free path and are located at the bottom of the universal curve leading (Figure 3.6). Therefore, He-I and He-II radiations are commonly used in ARPES measurements due to their high surface sensitivity. But primarily reason for He-I to be used in ARPES experiments is because of better momentum and energy resolution.

The two light sources described before are available in any laboratory systems due to their simple equipment models. On the other hand, limited photon energy range and low radiation flux of these sources prevent to perform more comprehensive experiments. To overcome this issue, synchrotron radiation is commonly used in the photoemission experiments. Synchrotron radiation is produced by the motion of accelerated electrons in a magnetic field inside the synchrotron ring. Equation of the motion for an electron moving under the magnetic field perpendicular to its velocity is given by the Lorentzian equation as:

$$\frac{d\vec{p}}{dt} = e \left(\vec{E} + \frac{\vec{v} \times \vec{B}}{c} \right) \quad (3.2)$$

where $\vec{p}$ and $\vec{v}$ are the electron momentum and the velocity vectors. As a result of such motion, the emitted light power is given by [13]:

$$P_e = \frac{2}{3} \frac{e^2 c}{R^2} \left(\frac{E}{mc^2} \right)^4 \quad (3.3)$$

where R is the radius of the circular orbit that electron moves. Such motion of the electron under magnetic field generates broad photon energy spectrum as seen in Figure 3.2. Therefore, the synchrotron radiation can be used in variety of spectroscopy, such as in ARPES and in core-level spectroscopy.

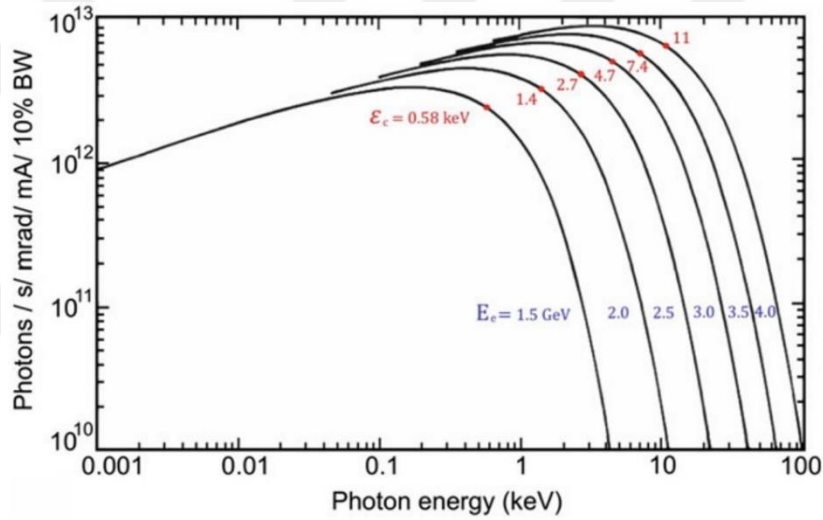


Figure 3.2. Power versus photon energy of synchrotron radiation.

3.3 Photoemission Spectroscopy

The fundamental of the photoemission spectroscopy is ejection of electrons from bound state as a result of absorption of radiation and escape of ejected electron into the vacuum from the solid as schematically shown in Figure 3.3. The photoemission process is described by photoelectric effect, first observed by Hertz and later explained by Einstein using quantum mechanics [1]. In Einstein's model, light consist of photons, which have energy of $E = h\nu$, where

h is the Planck constant and ν is the light frequency. If the energy of the photon exceeds the certain energy threshold, electrons are removed from the solid. The kinetic energy of the removed electron is given by:

$$E_k = h\nu - \phi - E_b \quad (3.4)$$

where ϕ is the work function, which is defined as a minimum energy for an electron to escape from surface of material into the vacuum. The E_b is the binding energy of the emitted electron relative to the Fermi level, and the E_k is the kinetic energy of the photoelectron. If equation 3.4 is always satisfied only $h\nu$ is smaller than $\phi + E_b$, electrons can escape from solid into the vacuum and travel towards the electron analyzer, which records the kinetic energy as a function of the photoelectron intensity or at a given emission, angle composing the photoemission spectrum as an example shown in the right panel of Figure 3.4.

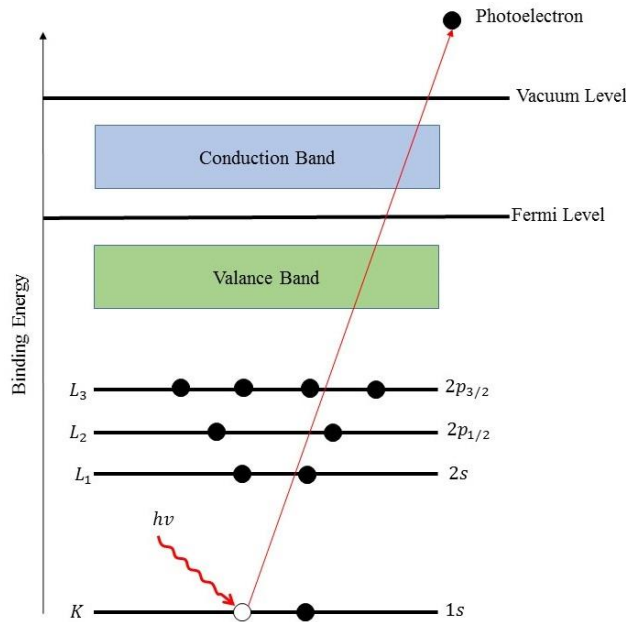


Figure 3.3. Schematic illustration of interaction of the light and core-level electrons producing the photoelectron.

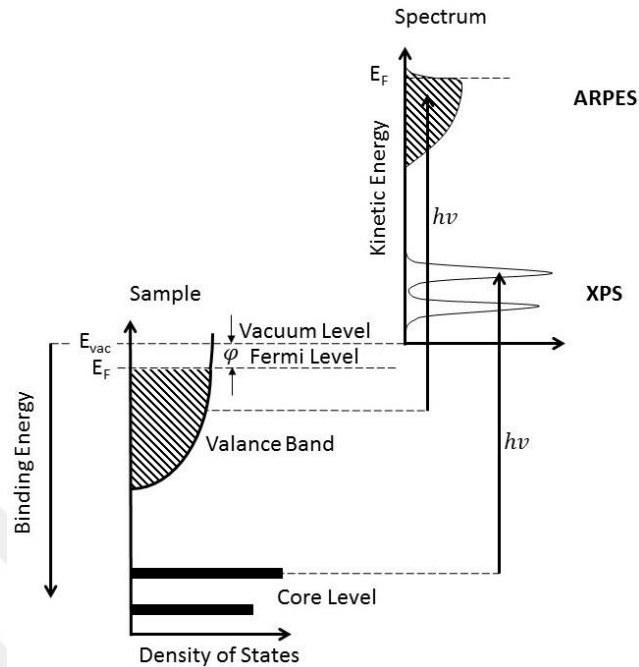


Figure 3.4. Schematic representation of the photoemission process. The left side of the figure shows the density of the electrons inside the solid as a function of the binding energy. The recorded photoemission spectra as a result of photoemission process is shown in the right side of the figure for XPS and ARPES [2].

The most common and simple model of the photoemission process is called three step model developed by Berglund and Spicer [4]. These three steps consist of:

- The electron is excited in to upper energy levels by absorption of a photon.
- The electron moves inside the solid towards the surface.
- The electron escapes from the potential barrier at the surface into the vacuum.

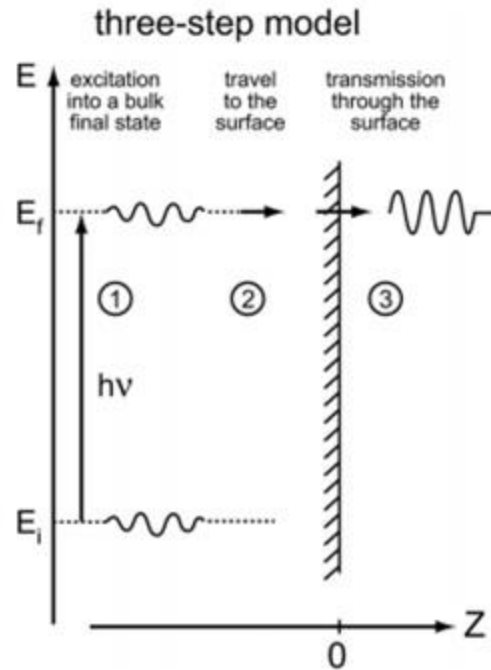


Figure 3.5. Three step model representation of photoemission process [4]

The first step is an optical excitation of an electron inside the solid where the electron is excited to a final state by the absorption of a photon.

In the second step, the excited photoelectron travels to the surface inside the solid. This can be treated as a classical transport process where the photoelectron undergoes inelastic scatterings resulting in change in its kinetic energy and momentum. On the other hand, non-scattered electrons escape the solid and give a sharp peak in the photoemission spectrum, which carries out important information about the electronic structure of solids. Whether or not photoelectrons reach the surface depends on the mean free path, which is the average distance that electron can travel inside the crystal without scattered. The mean free path strongly depends on the photoelectron kinetic energy as shown in Figure 3.6. This curve is called the universal curve because it does not depend significantly on the solid. An important conclusion from the universal curve is that the

photoemission technique is highly surface sensitive, resulting in the probing depth of only 5 Å to 20 Å.

The third step in the photoemission process is the escape of photoelectron into the vacuum. During this process only parallel component of the photoelectron momentum is conserved. This has important consequence for ARPES technique as discussed in the proceeding sections.

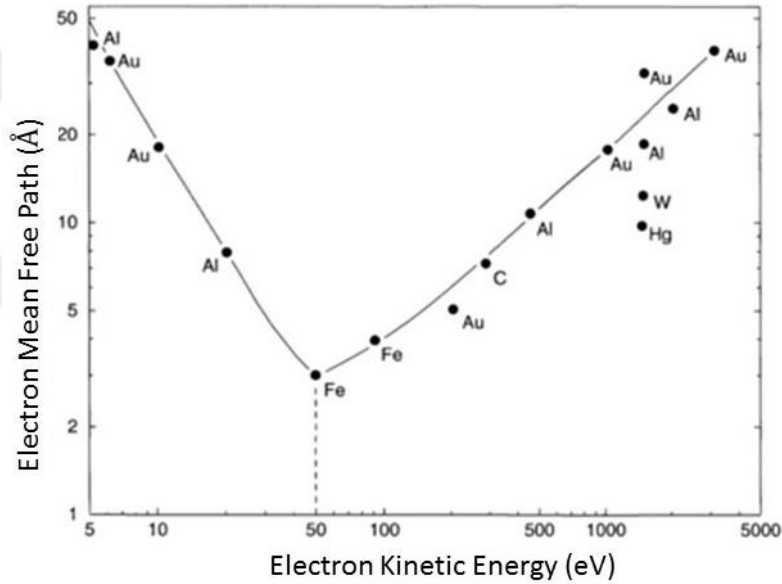


Figure 3.6. Universal curve for electron mean free path as a function of their kinetic energies [3].

3.4 Theoretical Description of the Photoemission Process

The transition probability of an electron from initial state to final state as a result of absorption of a photon can be expressed by the Fermi's golden rule as:

$$w_{f,i} = \frac{2\pi}{\hbar} \sum_n |\langle \psi_f^N | H_{PES} | \psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - \hbar\nu) \quad (3.5)$$

where, E_i^N and E_f^N are corresponding energies for the ground and the final state described by the wave functions ψ_i^N and ψ_f^N , respectively. The energy of the final state then can be represented as $E_f^N = E_f^{N-1} + E_k$, where E_f^{N-1} is the energy of the system with one electron removed. H_{PES} is interaction Hamiltonian between the electron and the photon, and it can be expressed in terms of electron momentum $\vec{p}$ and photon's electromagnetic vector potential $\vec{A}$ as:

$$H_{PES} = -\frac{e}{2m_e c} (\vec{A}\vec{p} + \vec{p}\vec{A}) \quad (3.6)$$

This term can be approximated by the dipole approximation $\Delta\vec{A} = 0$, which neglects the large variation of dielectric constant at the interface of the vacuum and the sample, as:

$$H_{PES} = -\frac{e}{m_e c} \vec{A}\vec{p} \quad (3.6)$$

The N-electron system wave function can be written as a Slater determinant of the outgoing electron wave function, ϕ_f^k , and the N-1 electron system wave function, ψ_f^{N-1} :

$$\psi_f^N = \mathcal{A}\phi_f^k\psi_f^{N-1} \quad (3.7)$$

where $\mathcal{A}$ is the antisymmetrizing operator, which is a linear operator making the wave functions asymmetric under the exchanged coordination. Hence, photoemission dipole matrix element can then be defined as:

$$M_{f,i}^k \propto \langle \phi_f^k | H_{PES} | \phi_i^k \rangle \quad (3.8)$$

As a result, the photoelectron intensity as a function of the kinetic energy at a momentum $\vec{k}$ is given by:

$$I(E_b) \propto \sum_n |M_{f,i}^k|^2 \sum_n |\langle \psi_f^{N-1} | \psi_i^{N-1} \rangle|^2 \delta(E_k + E_f^{N-1} - E_i^N - hv) \quad (3.9)$$

By using the commutation relation between the position operator x and the photoemission Hamiltonian H_{PES} , $[x, H_{PES}] = \frac{i\hbar\vec{p}}{m_e}$ and describing radiation field vector as $\vec{A} \sim A_0 \hat{\epsilon} e^{i(\frac{\omega}{c})\hat{n} \cdot \vec{x}}$, matrix element can be defined as:

$$M_{f,i}^k \propto \langle \phi_f^k | \hat{\epsilon} \cdot x | \phi_i^k \rangle \quad (3.10)$$

where $\hat{\epsilon}$ is unit vector along the polarization direction of the vector potential. The Equation 3.10 shows the important aspect that the photoelectron intensity depends on the initial state wave function and the momentum of the photoelectron as well as polarization of the incident light. Mathematically, a product of an even and odd function is zero, therefore, the matrix element also indicates that some transitions are allowed others could be forbidden. Let's consider the experimental condition given in Figure 3.7 for photoemission from $d_{x^2+y^2}$ initial orbital. In order to obtain non-zero photoelectron intensity, the matrix element has to be even function in the mirror plane of the experiment because of odd wave function is zero everywhere in the mirror plane. The photoemission intensity in the detector is also described as even parity plane wave $e^{i\vec{k} \cdot \vec{x}}$ with momentum $\vec{k}$ in the mirror plane. Therefore, $\hat{\epsilon} \cdot x | \phi_i^k \rangle$ has to be even for non-vanishing photoelectron intensity. Thus, in order to obtain non-zero photoelectron intensity there are two

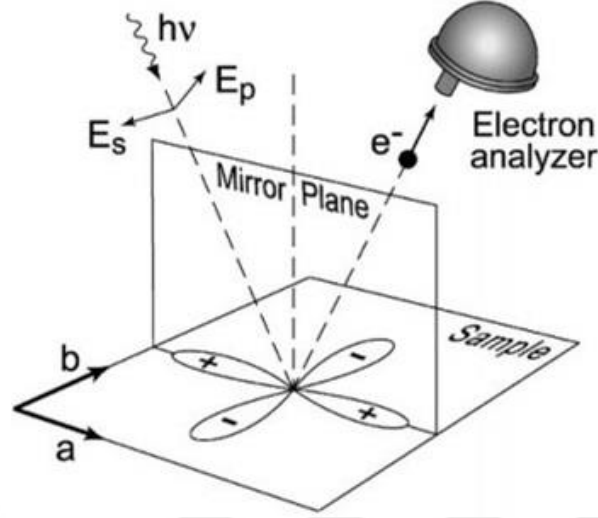


Figure 3.7. Schematic representation of photoemission geometry of $d_{x^2+y^2}$ orbit for s and p polarized light with respect mirror plane [19].

cases depending on the parity of the initial state: (i) if the initial state has the even parity with respect to mirror plane, light polarization vector $\vec{A}$ must also be even parity, which is p-polarized light ($\vec{A}$ is in plane); (ii) if the initial state has odd parity than light polarization vector $\vec{A}$ must be also odd, which is s-polarized light ($\vec{A}$ is normal to the mirror plane). In conclusion, based on the parity of the initial state, dipole selection rule can be summarized as:

$$\langle \phi_f^k | \vec{A} \vec{p} | \phi_i^k \rangle \begin{cases} |\phi_i^k\rangle \text{ is even} & \text{therefore } \langle + | + | + \rangle \Rightarrow \vec{A} \text{ is even} \\ |\phi_i^k\rangle \text{ is odd} & \text{therefore } \langle + | - | - \rangle \Rightarrow \vec{A} \text{ is odd} \end{cases} \quad (3.11)$$

$\vec{A} \vec{p}$ term in the matrix element preserves the crystal momentum during the ejection of the photoelectron. Therefore, such transition is called direct optical transition [18]. Furthermore, direct transition can only occur for a specific photon energy as illustrated, in Figure 3.8(a). This photon dependence of the optical transition allows to probe different energy bands by varying the photon

energy as shown in Figure 3.8(b). In the Figure 3.8(a), series of optical transitions are shown with the vertical arrows that each of them corresponds to the different photon energy. This is experimentally shown in Figure 3.8(b) that the *sp* direct transition peak shifts to lower binding energy with increasing photon energy due to the energy dispersion of the initial and final states.

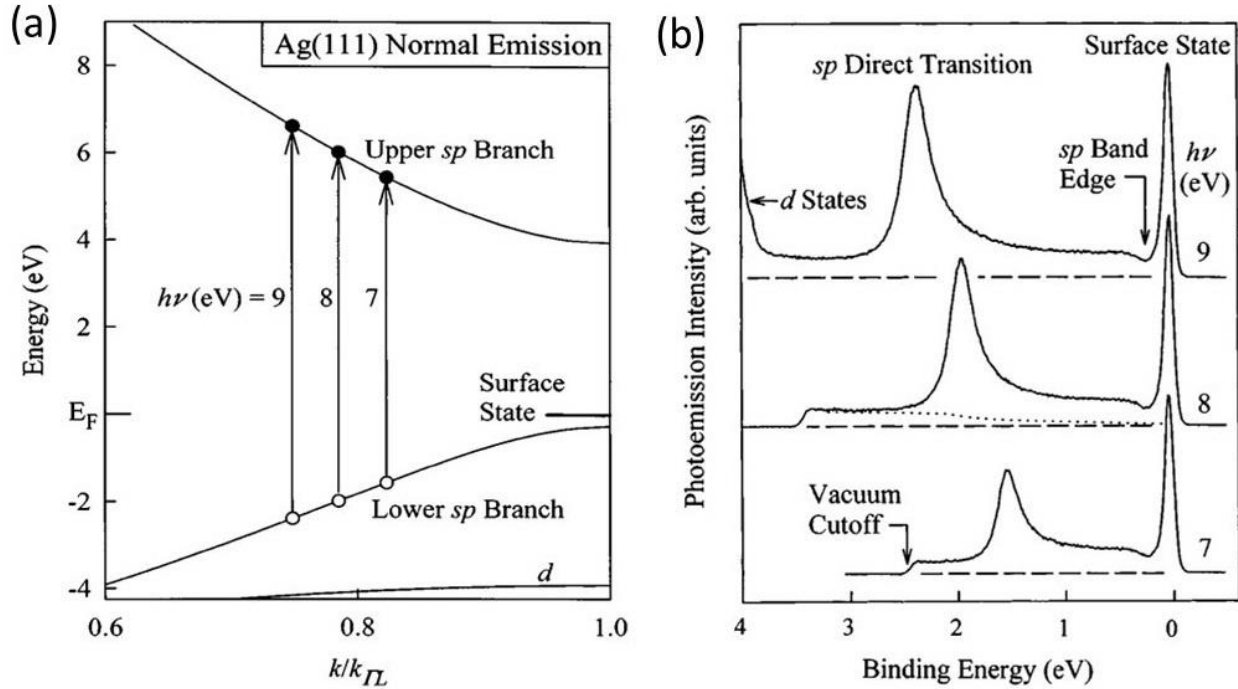


Figure 3.8.(a) Band structure of Ag along the [111] direction. Direct transitions are represented by vertical arrows for different photon energies. (b) Normal emission spectra from Ag (111) taken with 7, 8, and 9 eV photon energies. Dashed horizontal line represents the zero intensity [18].

3.5 Angle Resolved Photoemission Spectroscopy

Angle Resolved Photoemission Spectroscopy (ARPES) is experimental technique that can detect the electronic structures of solids. In particular, ARPES records the electron intensity versus the kinetic energy or the emission angle constructing either the Energy Dispersive Curve (EDC),

or the Momentum Dispersive Curve (MDC). The EDC and MDC give complementary information on the electronic structure of the solids.

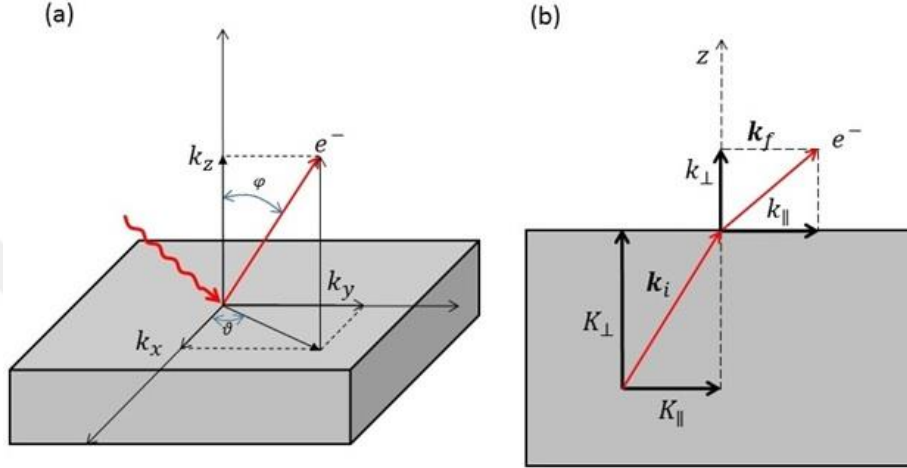


Figure 3.9.(a) 3D representation of components of the photoelectron momentum in the vacuum. (b) Parallel and perpendicular momentum of the photoelectron inside the solid and the vacuum. At the interface of the solid and the vacuum, parallel component of the photoelectron momentum is conserved.

The ARPES technique is based on principle of the conservation of the parallel component of the electron wave vector during the photoemission process. In the ARPES experiment, the momentum of the photon is relatively small compared to the size of the Brillouin zone and it can be neglected. Thus, we can write that:

$$\vec{k}_f + \vec{k}_i = \vec{G} \quad (3.12)$$

where $\vec{G}$ is reciprocal lattice vector and $\vec{k}_f$ and $\vec{k}_i$ are final and initial state momentum of the electron. The total momentum of the emitted electron inside the solid is given by:

$$K = \sqrt{2mE_{kin}}/\hbar \quad (K_{\parallel}^2 = K_x^2 + K_y^2, \quad K_{\perp} = K_z) \quad (3.13)$$

By using equation (3.13), and Figure 3.9(a), we can write down the components of the photoelectron momentum as,

$$k_x = \frac{1}{\hbar} \sqrt{2mE_{kin}} \cos \vartheta \sin \varphi \quad (3.14a)$$

$$k_y = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \vartheta \sin \varphi \quad (3.14b)$$

$$k_z = \frac{1}{\hbar} \sqrt{2mE_{kin}} \cos \varphi \quad (3.14c)$$

$$k_{\parallel} = K_{\parallel} = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \varphi \quad (3.14d)$$

where $k_{\parallel}$ and $K_{\parallel}$ are parallel components inside the sample and in the vacuum, respectively. The in-plane component of the photoelectron momentum can be obtained from the equation 3.14d by extracting the kinetic energy and the emission angle gained from the ARPES spectra recorded by the electron analyzer.

On the other hand, perpendicular component of the electron momentum is more complicated because it is not conserved due to the broken translational symmetry along z-axis and $k_{\perp}$ can be written for a given the inner potential V_o as:

$$k_{\perp} = \frac{1}{\hbar} \sqrt{2m(E_{kin} \cos^2 \varphi + V_o)} \quad (3.15)$$

3.6 ARPES: Current Applications

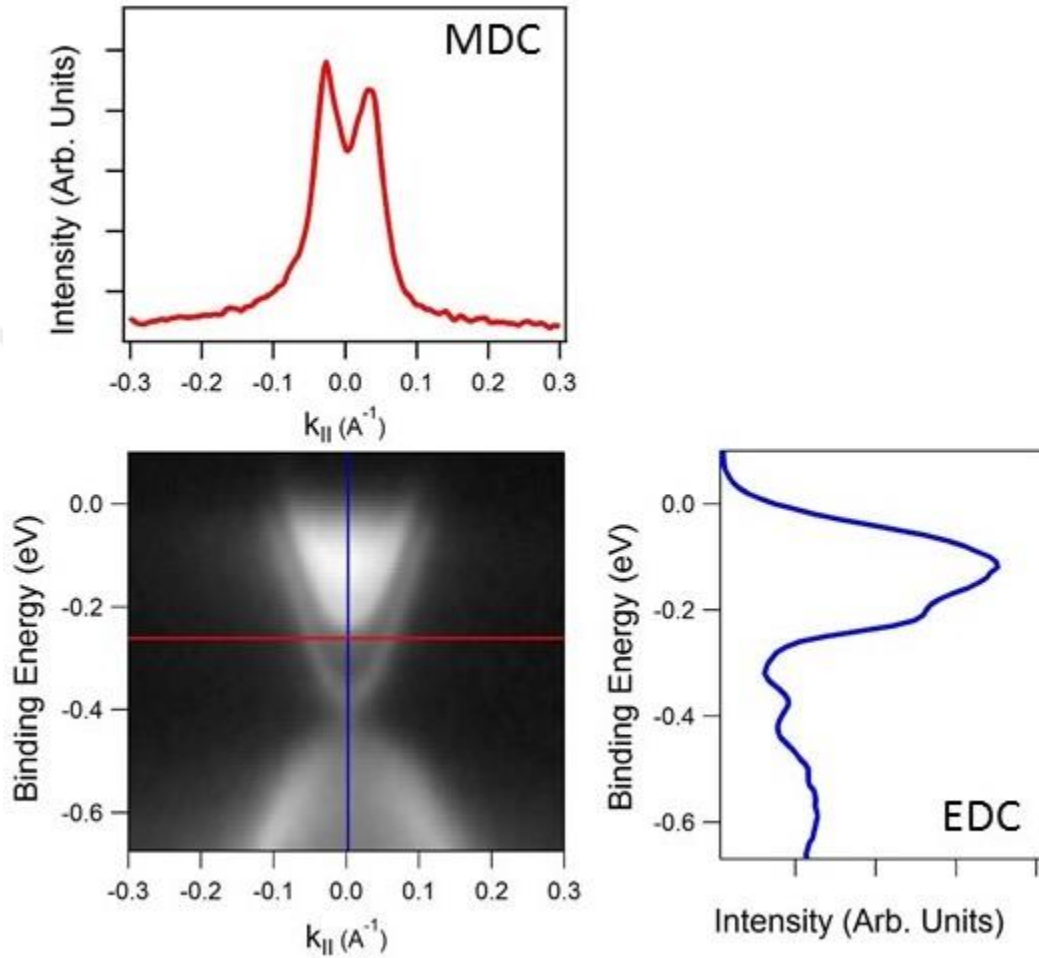


Figure 3.10. ARPES measurement taken from cleaved Bi_2Se_3 with 18 eV photon energy. Upper panel and right panel show the MDC and the EDC along the red and blue line, respectively.

In the early days of the photoemission spectroscopy, ARPES data were constructed by taking series of EDC spectra at different emission angles, which is achieved by rotation of the sample manually, and constructing 2D plot of intensity versus E and $k_{||}$. Recent advances in electron analyzers and 2D electron detection techniques now allows to measure such 2D plots of the electronic structure at fixed sample position. An example of the modern ARPES experimental

result is shown in Figure 3.10 taken from the cleaved Bi_2Se_3 crystal under the ultra-high vacuum condition at the U5UA beam line of the National Synchrotron Light Source (NSLS-I) at the Brookhaven National Laboratory (BNL). The spectrum consists of the parallel momentum of the photoelectron, which corresponds to the emission angle in the photoemission experiment setup, versus the binding energy of the photoelectron with respect to the Fermi level. The individual EDC spectra can be extracted from such 2D intensity plot by taking the slice of the photoelectron intensity at the fixed momentum as shown in Figure 3.10 (right panel) corresponding the horizontal blue line in the ARPES measurement. Furthermore, the MDC spectra can be also extracted along the red line as indicated in the Figure 3.10 at the binding energy of 280 meV. In the MDC plot, the photoelectron intensity versus the photoelectron momentum is scanned at the fixed energy, so that momentum versus the photoelectron intensity is constructed.

Furthermore, 2D construction of the Fermi surface is also possible with the ARPES measurement by recording electronic structure at different emission angle (k_y) and constructing the 2D plot of the intensity with respect to the k_x and k_y parallel momentum of the photoelectron at the Fermi energy. An example of the Fermis surface obtained from ARPES measurements is given in Figure 3.11(a) for $\text{FeTe}_{0.6}\text{Se}_{0.4}$ [11].

Another common usage of the ARPES is determination of the superconducting gap energy. It is well known phenomena in the condensed matter physics that there will be an energy difference between the Fermi levels of the normal and the superconducting states of the material. An example of the superconducting energy gap measurements by ARPES for $\text{FeTe}_{0.6}\text{Se}_{0.4}$ is shown in Figure 3.11 (b). EDCs are extracted from the Fermi surface of $\text{FeTe}_{0.6}\text{Se}_{0.4}$ as shown in Figure 3.11(a) for $\varphi=0^\circ$ (φ is the angle with respect to the k_x in order to indicate the position of the EDC on the Fermi surface). The EDC shows the temperature dependence that indicates energy shift to the lower

binding energy starting at 14.5 K suggesting that the critical temperature for the superconductivity is 14.5 K. In addition, EDC also allows to detect another sign of the superconductivity, which is the quasiparticle peak located around -3 meV binding energy below the Fermi level.

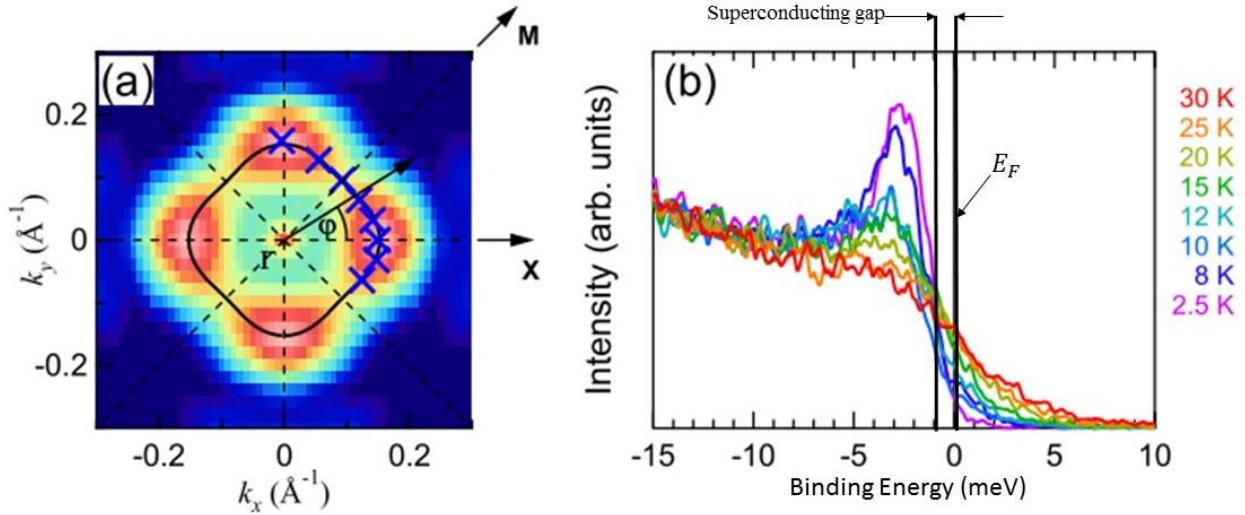


Figure 3.11.(a) Fermi surface of FeTe_{0.6}Se_{0.4} measured at 25 K. (b) Temperature dependence of EDC taken at $\phi=0^\circ$ at the Fermi level [11].

3.7 X ray photoemission spectroscopy (XPS)

XPS is a powerful technique to investigate the local electronic properties of the materials. From XPS we can learn the elemental composition, oxidation states of the elements and relative composition of the compounds in the surface region. In order to reach such information, photoelectron intensity versus kinetic energy and the emission angle have to be quantitatively analyzed. In XPS, photoelectron intensity depends on several factors:

- photoemission process.
- electron loss process due to interaction of the photoexcited electrons within the solid.

- instrument.

(i) Photoemission process is determined by the photoionization cross section of the specific core-level for a specific photon energy and experimental geometry (relative orientation of the photon polarization and the emission direction). It describes the probability of removing one electron from its bound state. The photoionization cross sections of electron subshells for different elements and for different photon energies have been calculated and are well known [16].

(ii) Electrons traveling inside the solid lose its energy due to the interaction with that solid. This will lead to reduction in the photoelectron intensity. The relationship between initial (I_0) and the final intensity (I) of photoelectrons after traveling the distance l is given in terms of inelastic mean free path (λ),

$$I = I_0 e^{-l/\lambda} \quad (3.16)$$

(iii) Instrumental factors include the electron detection efficiency of the electron analyzer, x-ray flux.

The spectra are often recorded as the photoelectron intensity versus the kinetic energy. The kinetic energy can be easily converted to the electron binding energy by using equation 5. One important information from XPS is the peak area that is used to calculate atomic concentrations in a compound. This is done by fitting a line shape to a recorded core-level photoemission spectrum. A common line shapes are Gaussian and Lorentzian line shapes. Lorentzian line shape has extended tails in the lower and the higher binding energy sides of the main peak compared to the Gaussian line shapes as seen in Figure 3.12. Mixed Lorentzian and Gaussian line shapes are often used to fit the XPS peak because core-hole life time broadening is best represented by a Lorentzian line shape, while the experimental equipment such as the x-ray radiation source and the electron

analyzer contribute to broadening best described by the Gaussian line shape [3]. The asymmetric Doniach-Sunjc (DS) line shape is used for core-level peaks from metallic samples [6]. Such have asymmetric line shapes occurs in metals due to the screening of electrons by conduction band.

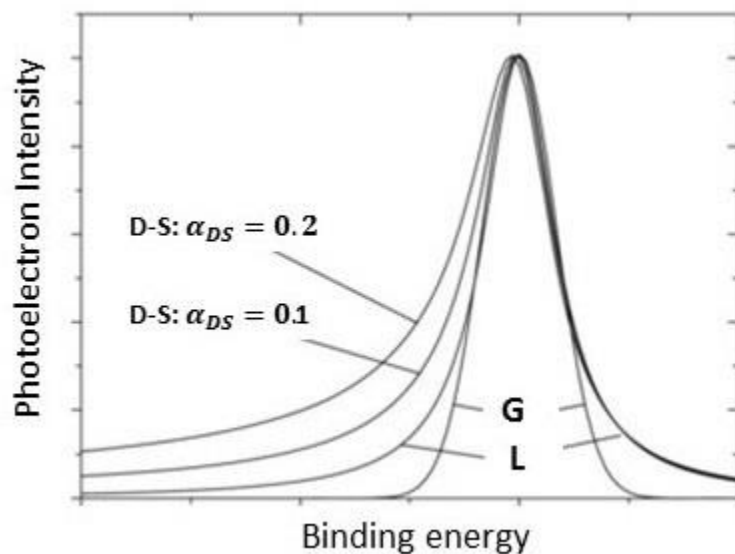


Figure 3.12. Common line shapes used in XPS peak fitting. DS line shape is drawn for different asymmetry parameter (α_{DS}). G and L represent the Gaussian and Lorentzian line shapes, respectively. [6].

Another important procedure used in XPS peak analysis is estimating and removing the photoelectron background. This background arises mostly from the inelastic scattering of electrons with surrounding atoms, which leads to increase in the background on the higher binding energy side of each photoemission peak. Several types of the background shapes are used. The simplest is the linear background line shape. If there is no intensity difference between the lower and the higher binding energy sides of the peak, linear background line shape can be used. However, core-level photoelectron intensities suffer from the inelastic scatterings that lead to higher background

intensity on the higher binding energy sides of the peaks (Figure 3.13). For this reason, Shirley and Tougaard background types are introduced to subtract more reliable background from the XPS peak as seen in Figure 3.13. Shirley type of the background assumes that the background intensity at the any energy is proportional to the total peak area only above that energy. Furthermore, Tougaard background is based on the probability of an electron to undergo energy loss event contributing the spectral background, and this probability is called energy loss cross section.

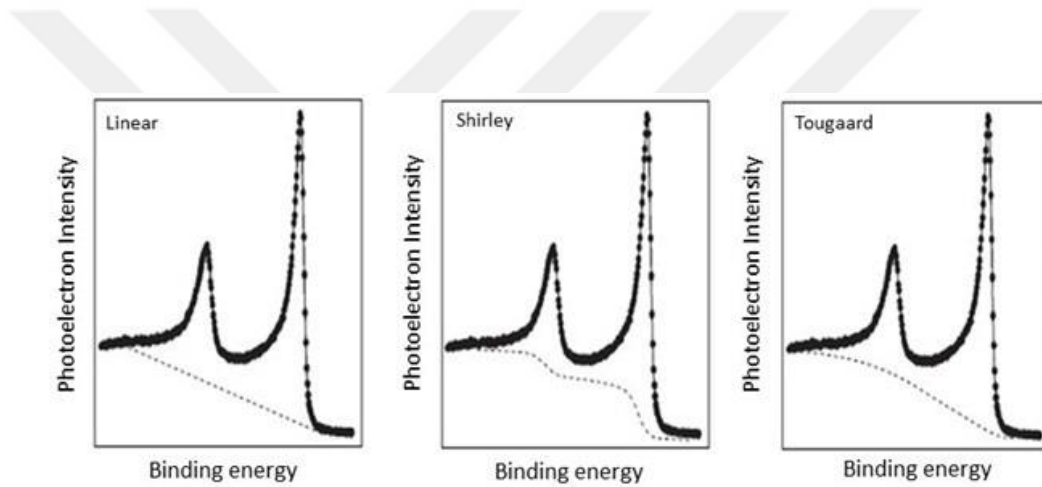


Figure 3.13. XPS peak fitting background line shapes [5].

Once the right background and line shape are applied, numerous information about the sample can be gained from the XPS measurements. One of use of using XPS is to compute relative stoichiometric ratios of elements within the sample. This can be calculated by using the peak areas, i.e. $A_x B_y$ sample by:

$$\frac{x}{y} = \frac{I_A \sigma_B}{I_B \sigma_A} \quad (3.17)$$

where I_A , I_B are photoelectron intensities of specific core-levels that belong to element A and B, respectively and σ_A , σ_B are their corresponding photoionization cross-sections of specific core-levels at specific photon energies.

Another important quantity obtained from fitting the photoemission spectra is the full width at half maximum (FWHM). Change of the FWHM can be an indicator for presence of the different chemical states or change of the chemical bonds between the atoms. The measured FWHM of the photoemission peak is determined by the natural line width of the peak and by experimental contribution. Therefore, total FWHM (Γ_{total}) is given by:

$$\Gamma_{TOTAL}^2 = \Gamma_{x-ray}^2 + \Gamma_{life\ time}^2 + \Gamma_{analyzer}^2 \quad (3.18)$$

Experimental contribution to the FWHM comes from the x-ray line width (Γ_{x-ray}), which is 0.85 eV for Al K_α , and the resolution of the electron energy analyzer ($\Gamma_{analyzer}$) as discussed in the previous chapter. These quantities do not change from one sample to another unless the x-ray source or the slits and the pass energy of the electron analyzer are changed. Therefore, change in the FWHM is usually related to change in natural line width of the core-levels, which can carry important information about the sample.

Contribution to the natural line width of the core-level included: (i) momentum broadening related to chemical bonding length between the atoms, (ii) screening of the electrons due to the conduction band, and (iii) final state effect, which arises from the radioactive or nonradioactive decay of the core-hole generated after electron emitting into the vacuum [14-15].

3.8 X-ray Diffraction

X-ray diffraction (XRD) method is widely used tool to determine, the crystal structure, the lattice parameters, the strain and the grain size of solids. XRD is based on the relationship between

the direction of the incident and the scattered x-ray waves. This relationship is known as the Bragg's law, and it is illustrated in Figure 3.14. Such relationship is first introduced by Sir W.H. Bragg and his son Sir W.L. Bragg to explain why the cleaved faces of crystals shows to reflect x-ray beams only at certain angles [12].

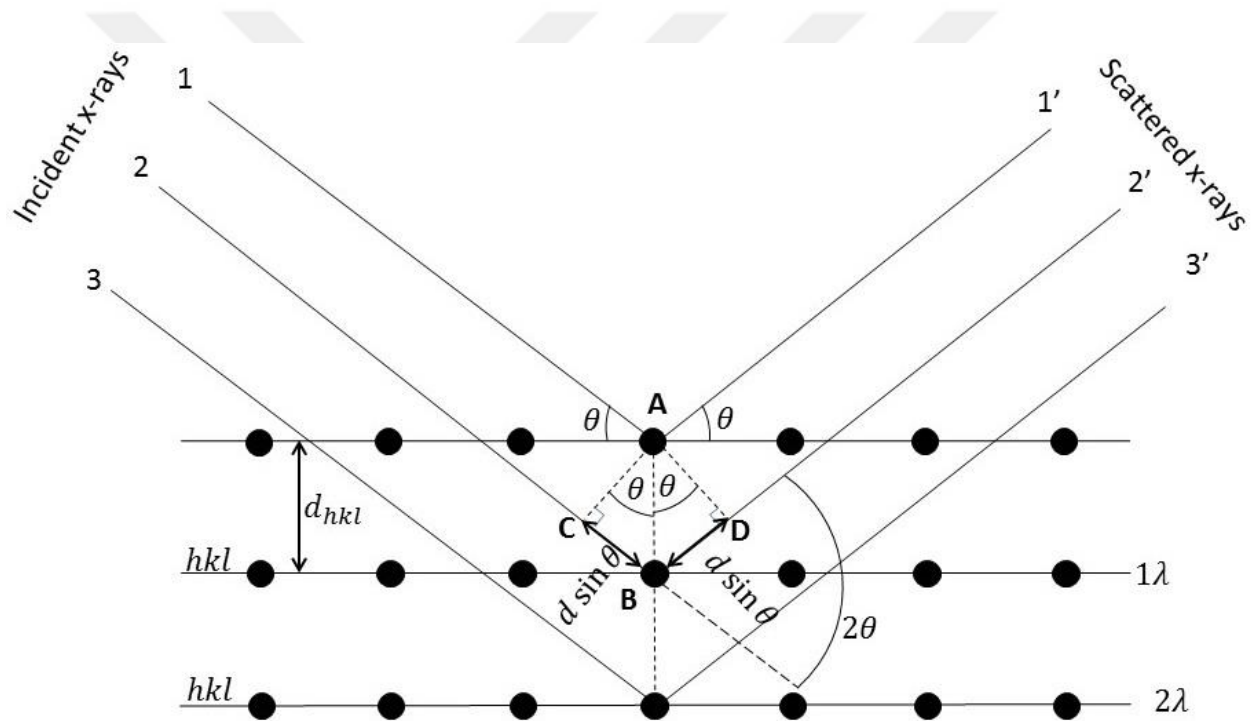


Figure 3.14. Diffraction of x-rays from atomic planes [17].

The Bragg's law is given by:

$$n\lambda = 2d_{hkl} \sin \theta \quad (3.19)$$

where, λ is the wave length of the incident x-ray beam, d_{hkl} is the distance between atomic layers, h, k, l are Miller indices, n is an integer representing the order of the diffraction peak and

θ is the angle between surface normal and reflected x-ray beam. The idea behind of the Bragg's law is that when waves interact with atomic layers spaced by d_{hkl} , there is a path difference of $2d_{hkl} \sin \theta$ as seen in Figure 3.14. If this distance is integer multiple of a wavelength, waves will interface constructively producing a reflected x-ray beam. On the other hand, a destructive interface occurs for out of phase combination of the scattered x-rays, which results in zero intensity in the XRD data.

Inter atomic layer spacing d_{hkl} can be calculated from equation 3.19 depending on the diffraction angle, and it is straight forward to calculate lattice parameters of crystal structure by using XRD data. For example, for cubic and hexagonal structures, “a” and “c” lattice constant can be computed by [20]:

$$\frac{1}{d_{hkl}} = \frac{h^2 + k^2 + l^2}{a^2} \quad (\text{cubic}) \quad (3.20a)$$

$$\frac{1}{d_{hkl}} = \frac{4}{3} \left(\frac{h^2 + hk + l^2}{a^2} \right) + \frac{l^2}{c^2} \quad (\text{hexagonal}) \quad (3.21b)$$

Furthermore, it is also possible to estimate the crystallite size by using the Scherrer equation introduced by Paul Scherrer [3.22]. Equation described the connection between the XRD peak width and the crystallite size and it is given by:

$$B(2\theta) = \frac{K\lambda}{L \cos \theta} \quad (3.22)$$

where B is XRD peak width due to crystallite size and L is crystallite size. K is the Scherrer constant, which shows dependence on crystal structure and the method for determination of XRD peak width. Values of K and excellent review of this method can be found in Reference 12. As

seen from the above equation, crystallite size is inversely proportional to peak width. This is important tool to estimate the crystallite size.

3.9 References

1. H. Hertz, *Annalen der Physik* 267 (8): S. 983–1000 (1887).
2. F. Reinert and S. Hüfner, *New J. Phys.* 7, 97 (2005).
3. S. Hüfner, *Photoelectron Spectroscopy: Principles and Applications*, Springer-Verlag, Berlin (1995).
4. C. N. Berglund and W. E. Spicer, *Phys. Rev. Vol. 4A*, p. A1030 and 1044 (1964).
5. P. van der Heide, *X-Ray Photoelectron Spectroscopy: An Introduction to Principles and Practices*, Wiley, 1 edition (2011).
6. S. Hofmann, *Auger- and X-Ray Photoelectron Spectroscopy in Materials Science: A User-Oriented Guide*, Springer, (2013).
7. C. R. Brundle, A. D. Baker, *Basic concepts of x-ray photoelectron spectroscopy*, Academic Press (1979).
8. J. R. Shallenberger, D. A. Cole, S. W. Novak, R. L. Moore, M. J. Edgell, S. P. Smith, C. J. Hitzman, J. F. Kirchhoff, E. Principe, S. Biswas, R. J. Bleiler, W. Nieveen, K. Jones, *Int. Conf. Ion Implantation Technology Proc.* pp 79–82 (1998).
9. D. F. Mitchell, K. B. Clark, J. A. Bardwell, W. N. Lennard, G. R. Massoumi, and I. V. Mitchell, *Surf. Interface Anal.* 21, 44 (1994).
10. J. Sanchez-Barriga, M. R. Scholz, E. Golias, E. Rienks, D. Marchenko, A. Varykhalov, L. V. Yashina, and O. Rader, *Phys. Rev. B* 90, 195413 (2014).
11. K. Okazaki, *J. Phys. Conf. Ser.* 449, 012019 (2013).
12. W. H. Bragg, W. L. Bragg, *Proc R. Soc. Lond. A* 88 (605): 428–38 (1913).
13. S. Mobilio, F. Boscherini, C. Meneghini, *Introduction to Synchrotron Radiation*, Springer (2015).
14. P. S. Bagus, E. S. Ilton, and C. J. Nelin, *Surf. Sci. Rep.* 68, 273 (2013).
15. T. M. Duc, C. Guillot, Y. Lassailly, J. Lecante, Y. Jugnet, and J. C. Vedrigne, *Phys. Rev. Lett.* 43, 789 (1979).
16. J. J. Yeh, I. Lindau, *At. Data Nucl. Data Tables* 32, 1 (1985).
17. http://www.chem.sc.edu/faculty/zurloye/xrdtutorial_2013.pdf
18. T. Miller, W. E. McMahon and T.-C. Chiang, *Phys. Rev. Lett.* 77, 1167 (1996).
19. A. Damascelli, Z. Hussin, and Z.-X. Shen, *Rev. Mod. Phys.* 75, 473 (2003).
20. http://www.chem.sc.edu/faculty/zurloye/xrdtutorial_2013.pdf
21. P. Scherrer, *Nachr. Ges. Wiss. Göttingen* 26, 98-100 (1918).
22. J. I. Langford, and A. J. C. Wilson, *J. Appl. Cryst.* 11, 102-113 (1978).

4. Crystal and Electronic Structure of MBE grown Bi₂Se₃

Topological Insulator

4.1 Introduction

Topological Insulators (TIs) possess inverted and insulating bulk states, while a very special metallic state emerges on the sample surfaces due to strong spin-orbit coupling [1]. The electrons on the surface of TIs obey the massless Dirac equation that satisfies: $H = \vec{v}\vec{\sigma}\vec{q}$, where $\vec{v}$ is velocity, $\vec{\sigma}$ Pauli spin matrix and $\vec{q}$ is electron momentum [2]. Such equation shows that energy of the the electrons on the surface of TIs disperses linearly with respect to their momentum forming the 2D Dirac cone. Among the TIs, Bi₂Se₃ is one of the most promising TI due to its large bulk band gap of 300 meV and well resolved Dirac like surface states on photoemission experiments [1, 2]. Therefore, the unique surface states of Bi₂Se₃ have been intensively investigated [3-6].

The gapless surface states of Bi₂Se₃ are located within the energy gap formed by the inverted Bi 6p and Se 4p orbitals. As indicated with dashed lines in Figure 4.1(a), the band inversion between Bi 6p and Se 4p orbitals occur in four stages driving Bi₂Se₃ from normal state to inverted state. In the first stage, Bi 6p orbital has higher binding energy than Se 4p orbital in the atomic state. Chemical interaction between Bi 6p orbital and Se 4p orbital leads to formation of bounding and anti-bounding states resulting in pushing Bi 6p orbital to higher binding energy and lowering the Se 4p orbital binding energy in the second stage. In the third stage, the crystal field splitting induces the separation between P_z orbital and P_{x,y} orbitals resulting in Bi 6P_z orbital having higher binding energy, while Se 4P_z orbital having lower binding energy. In the final stage, Se 4P_z and Bi 6P_z orbitals are inverted by strong spin-orbit coupling turning system from a band insulator into a topological insulator. Schematic energy band structure of the normal (insulating) and the

inverted (topological) states in Bi_2Se_3 are presented in Figure 4.1(b). The band inversion is indicated by the color exchange between the bottom of Bi 6p orbital and the top of Se 4p orbital. Additionally, the surface states illustrated with solid black line in Figure 4.1(b) emerges within the inverted bulk band gap as a result of the band inversion. These states have strong Bi P_z and Se P_z contribution and non-negligible Bi and Se $P_{x,y}$ contribution [14].

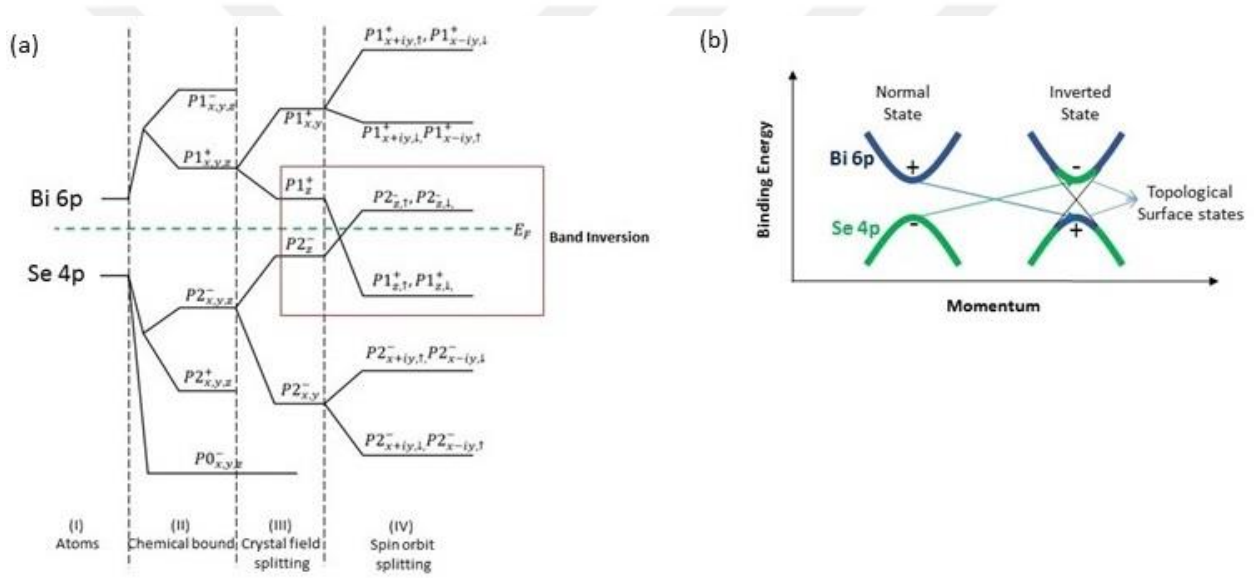


Figure 4.1.(a) Schematic representation of the band inversion in Bi_2Se_3 . **(b)** Schematic illustration of the bulk conduction band and the bulk valence band in the normal and inverted states. Plus, and minus represent the band parities.

It is possible to transform inverted state in Bi_2Se_3 back to the normal state by altering the lattice parameters of Bi_2Se_3 [7]. Hence, the crystal structure of Bi_2Se_3 is another important feature. Bi_2Se_3 has a hexagonal crystal structure formed by stacking of quintuple layers (QL), which are weakly connected to each other by van der Waals interaction (Figure 4.2). One single QL of Bi_2Se_3 has the stacking order of Se and Bi atomic layers are $-\text{[A(Se1)-B(Bi1)-C(Se2)-A(Bi1')-}$

B(Se1')– along the z direction [1]. The “c” and “a” lattice parameters of Bi_2Se_3 are 28.65 Å and 4.14 Å, respectively.

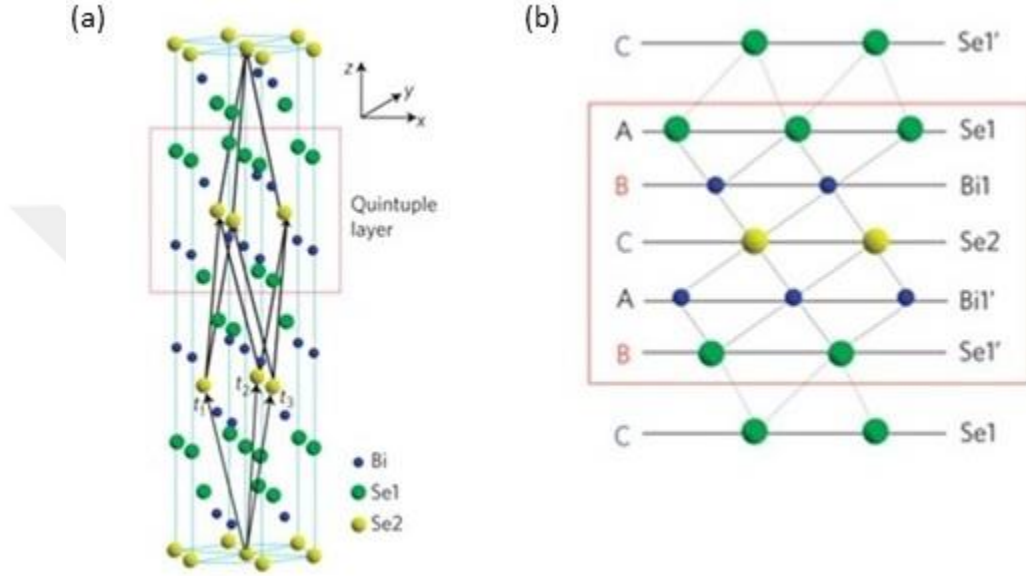


Figure 4.2.(a) Crystal structure of Bi_2Se_3 . (b) Side view of the crystal structure [1].

Here, we investigated the topological surface states and the crystal structure of Bi_2Se_3 films grown on Al_2O_3 (0001) substrate. We will first confirm the high crystal quality of molecular beam epitaxial grown (MBE) Bi_2Se_3 films by low energy electron diffraction (LEED), x-ray diffraction (XRD) and x-ray photoemission spectroscopy (XPS) techniques. Then, we will present our angle resolved photoemission spectroscopy (ARPES) measurements performed on Bi_2Se_3 films with different thicknesses.

4.2 Experiment

Number of the growth techniques, including molecular beam epitaxy (MBE) and pulsed laser deposition (PLD), have been employed on the growth of high quality Bi_2Se_3 films on different substrates such as $\text{Al}_2\text{O}_3(0001)$ and $\text{Si}(111)$ [8-14]. A recent work in the literature introduced the two-step growth method to improve the crystal quality of the MBE grown films [14]. In this method, few QL of TI are deposited at relatively low temperature, usually around 120 °C, then the film is heated to temperature between 220 °C to 300 °C for deposition of extra material. In the second stage, substrate temperature is chosen above the melting point of Se to prevent excessive amount of Se in the film because growth takes place under the Se rich condition. Additionally, it is found that annealing the samples for about 30 minutes after at the growth temperature promotes the surface quality [14].

In our work, we used MBE method to grow Bi_2Se_3 films on $\text{Al}_2\text{O}_3(0001)$ substrate in our work. Growth was done in the MBE chamber with a base pressure of 2×10^{-9} torr. Prior to growth, $\text{Al}_2\text{O}_3(0001)$ substrates were annealed at 650 °C for 2 hours and then annealed at 850 °C for another 30 minutes to have atomically flat substrate surface with free contamination. High purity Bi (99.999%) and Se (99.999%) sources were evaporated from the resistively heated crucibles at 528 °C and 207 °C, respectively. The source temperatures were measured by a thermocouple wires attached at the bottom of the crucibles. Quartz crystal microbalance sensor was used to measure the source evaporation rates. It is measured to be 22 Å/min and 1.85 Å/min for Se and Bi sources, respectively. In our work, we followed two-step growth method where a single QL of Bi_2Se_3 was deposited at 115 °C and followed deposition at 225 °C. After the film growth, samples are rapidly transferred to the photoemission chamber to perform XPS and ARPES. Gamma Data's Scienta SES-100 analyzer were used to record spectra. PSP's TX400 X-ray Source was used to generate

Al K_{α} x-rays with energy of 1485.6 eV for XPS and SPECS's UVS20-A UV-lamp was used to generate He I_{α} with energy of 21.2eV for ARPES measurements. All XPS data were obtained with the same total experimental resolution of 0.9 eV. In addition, bulk crystal structure analysis was performed by XRD with Cu K_{α} on Bruker's D2 Phaser instrument. In order to further investigate crystal structure, LEED experiment was performed in different UHV chamber. To perform such experiment on a film grown in the different UHV chamber, the film was capped with 10 nm Se, and load to another UHV chamber where the film was annealed until the sharp LEED pattern was visible.

4.3 Results

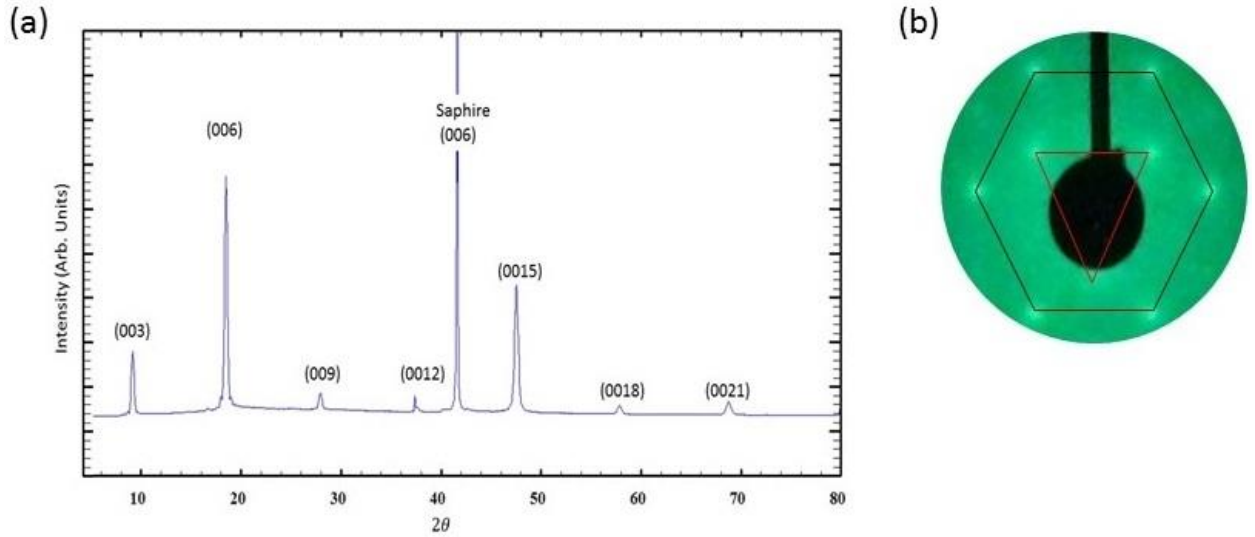


Figure 4.3.(a) XRD pattern of 22 QL Bi_2Se_3 . Scans are taken with a Cu anode ($\lambda = 1.54 \text{ \AA}$). (b) LEED pattern of 22 QL Bi_2Se_3 obtained with 174 eV electron energy.

In Figure 4.3(a), X-ray diffraction pattern of 22 QL Bi_2Se_3 grown on $\text{Al}_2\text{O}_3(0001)$ substrate is presented. XRD pattern consists of sharp $(00l)$ peaks indicating that film growth is c-axis oriented. We calculated the c lattice parameter to be $28.6 \text{ \AA}$, which is consistent with literature

value [15]. In addition, the LEED pattern of Bi₂Se₃ grown on Al₂O₃ (0001) substrate shows six-fold pattern indicating the high crystal quality of the film (Figure 4.3(b)).

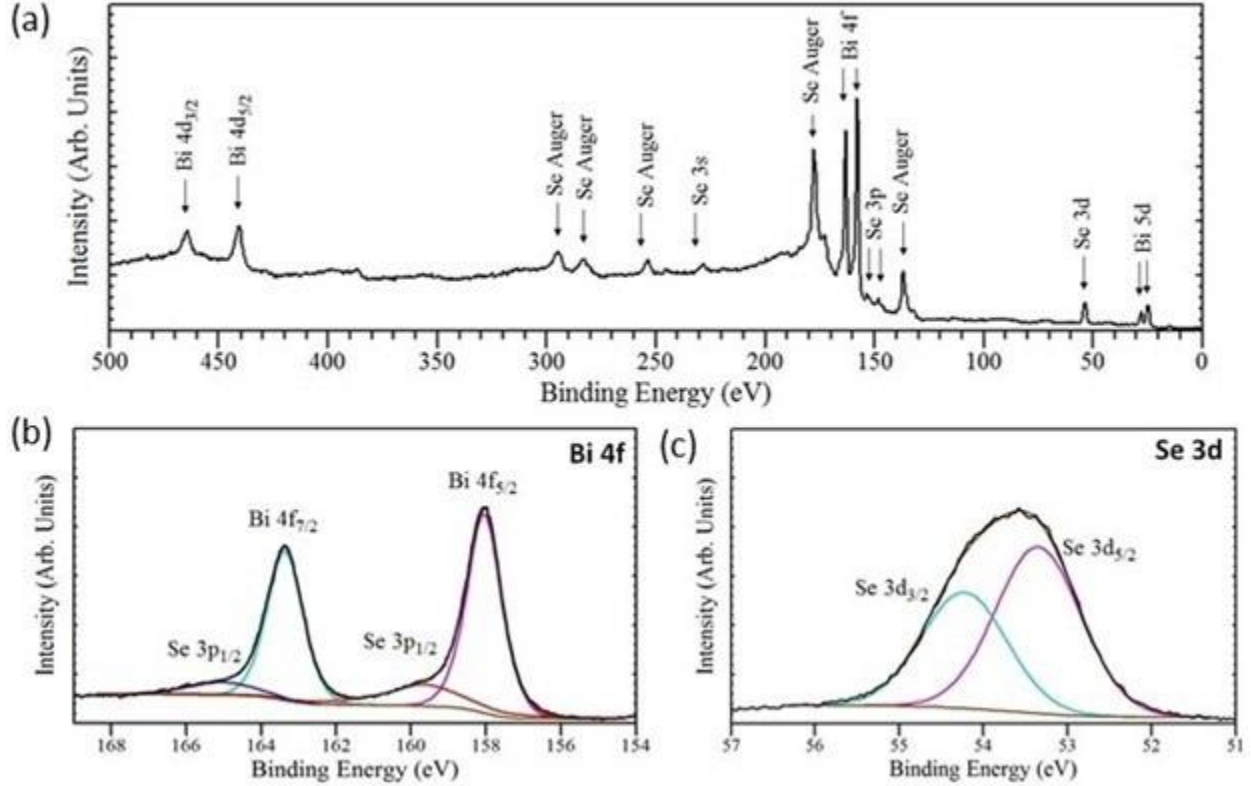


Figure 4.4. XPS study of the MBE grown 22 QL of Bi₂Se₃ thin film on Al₂O₃(0001) substrate. **(a)** The survey XPS spectrum 22 QL of Bi₂Se₃. **(b)** Bi 4f and **(c)** Se 3d. All the spectra were recorded at the room temperature with 1485.6 eV radiation. Purple and cyan colored lines represent the linear combination of Gaussian and Lorentzian fitting line shapes. Brown line represents the Shirley type background.

We proceed on our work by performing XPS measurements to investigate the chemical environment of the MBE grown Bi₂Se₃ films on Al₂O₃ (0001) substrate. The survey spectrum of 22 QL Bi₂Se₃ film reveals the contamination free sample by exhibiting the core-levels and the Auger peaks of only Bi and Se (Figure 4.4(a)). Bi 4f shows two prominent peaks corresponding to the spin orbit split states of 4f_{7/2} and 4f_{5/2} located at 158.1 eV and 163.4 eV binding energies, respectively (Figure 4.4(b)). Spin-orbit splitting energy of Se 3d is smaller than the total

experimental resolution leading to observe an overlap of Se 3d_{5/2} and 3d_{3/2} peaks (Figure 4.4(c)). The fitting result gives Se 3d_{5/2} and 3d_{3/2} binding energies to be 54.2 and 53.3 eV, respectively. The binding energies of each core-levels obtained in our work are in good agreement with the literature values [16]. In addition, Bi 4f shows 1.1 eV energy shift to lower binding energy, while Se 3d has 2.2 eV shift to higher binding energy as compared to the pure bulk Bi and Se binding energies, respectively. These energy shifts indicate that Bi behaves as an electron donor, while Se is an electron acceptor. Moreover, two additional peaks were observed in the higher binding energy sides of the Bi 4f peaks, which are Se 3p_{3/2} and 3p_{1/2} peaks located at 159.3 eV and 165 eV binding energies, respectively. Stoichiometry of the film was calculated for the photoionization cross section 0.3236 for Bi 4f and 0.031 for Se 3d for a specific photon energy of 1486 eV. The Se to Bi atomic ratio is found to be 1.47, which is in close agreement with the expected value of 1.5.

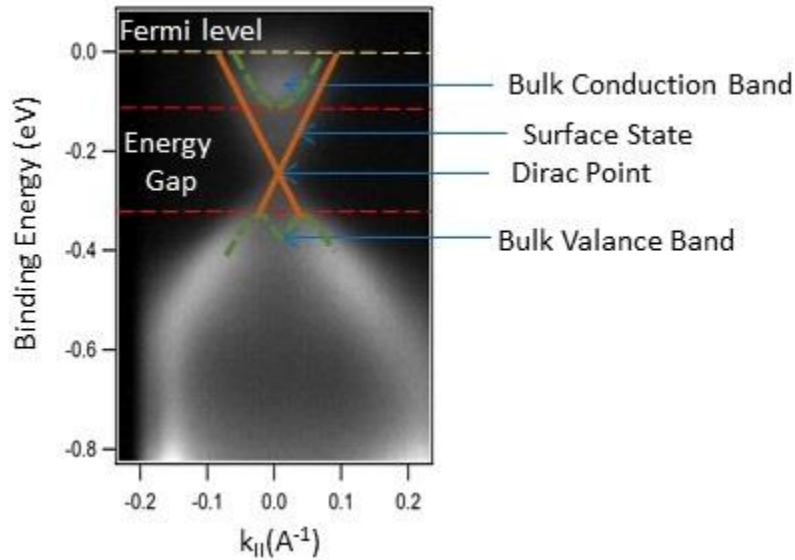


Figure 4.5. Electronic structure of 10 QL Bi₂Se₃ taken with 21.2 eV photon energy along the Γ -M direction at the room temperature. Thick orange line represents to surface states and dashed green lines indicate the bulk bands. Fermi level is shown by dashed yellow line.

Up to this point, we confirmed the high crystal quality of our MBE grown Bi_2Se_3 films on $\text{Al}_2\text{O}_3(0001)$ substrate. We proceed on our discussion by presenting the ARPES measurement in Figure 4.5 to reveal the unique electronic structure of Bi_2Se_3 . Topological surface states (TSSs) of Bi_2Se_3 exhibits their distinct feature by forming the Dirac point at Γ (000) and at 230 meV binding energy indicating the linear dispersion of the surface states as represented by orange lines in Figure 4.5. In addition, we can also resolve the bulk conduction and the valance bands separated by an energy gap of ~ 200 meV, which is measured from top of the bulk valance and the bottom of the bulk conduction band as indicated with the dashed green lines in Figure 4.5. Hence, we confirmed that our MBE grown Bi_2Se_3 films on $\text{Al}_2\text{O}_3(0001)$ substrate have the characteristics of TIs by displaying the Dirac like surface states and the bulk band gap.

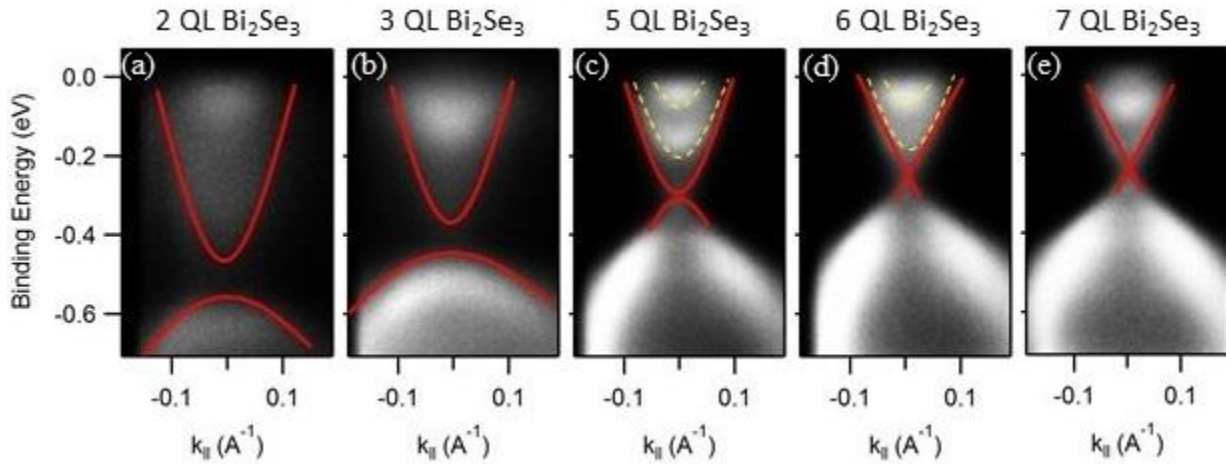


Figure 4.6.(a-e) Thickness dependence ARPES 2D intensity of Bi_2Se_3 . Solid red lines represent the evolution of gapless surface state. The dashed yellow lines and the solid red lines indicate the Rashba states and the surface states, respectively. Spectra were collected along with 21.2 eV photon energy the along the Γ -M direction at the room temperature.

We extended our study to investigate the film thickness effect on the electronic structure of Bi_2Se_3 . In Figure 4.6(a-e), we presented ARPES measurements obtained from the samples in

the thickness range from 2QL to 7QL. An energy gap of ~ 100 meV is observed at the Dirac point of 2QL of Bi_2Se_3 films. This energy gap originates from the hybridization of the surface states at the top and at the bottom of the film [17]. Increase in the thickness results in the suppression of the gap due to the weakened interaction between the surface states located at sample bottom and top. We further increased thickness to 5 QL where we can see notable changes on the electronic structure of Bi_2Se_3 . At 5 QL, surface states show fairly linear dispersion compared to the thinner films. In addition, Rashba type of the bulk band splitting started to appear at 5 QL, which is due to the potential difference between the bottom and the surface of the sample [17]. Finally, 6 QL film has vanished energy gap forming the Dirac point at Γ (000) and at 290 meV binding energy indicating the linear dispersion of the surface states as represented with straight red lines in Figure 4.6(d). We did not observe any alteration on the electronic structure of Bi_2Se_3 for thicker film of 7 QL except for shifting of the Dirac point to lower binding energy around 40 meV.

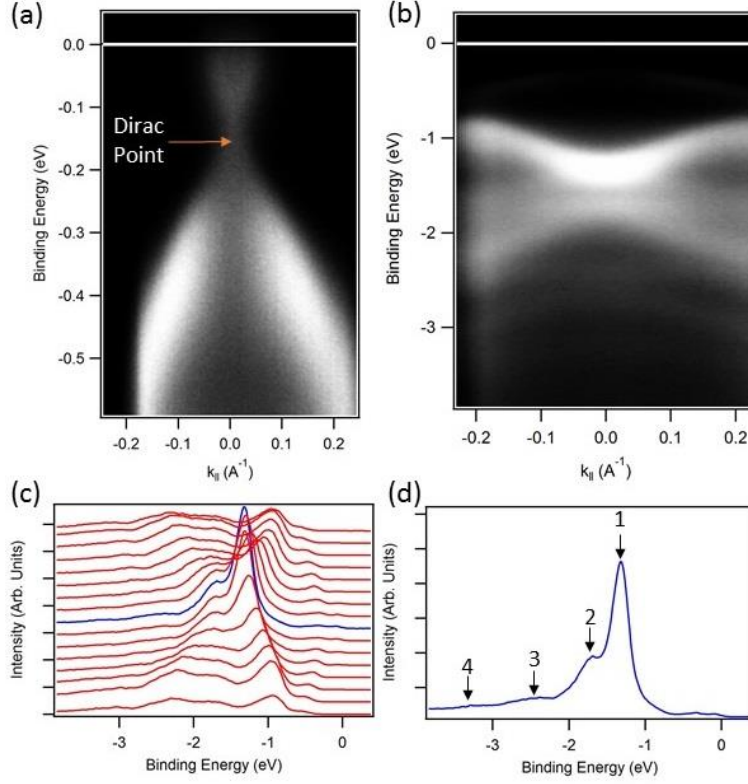


Figure 4.7. (a) ARPES 2D intensity of 22 QL of Bi_2Se_3 thin film. (b) Wider energy map of the electronic structure of Bi_2Se_3 . (c) Energy dispersive curves (EDCs) at different $k_{||}$, (d) EDC at the Γ (000) point. Thick white line represents the Fermi level, and arrows in (d) show the bulk bands. ARPES spectra were recorded along the Γ -M direction with 21.2 eV photon energy and at the room temperature.

In order to resolve further effect of the film thicknesses on the electronic structure of Bi_2Se_3 , we presented ARPES 2D intensity of 22 QL Bi_2Se_3 film in Figure 4.7(a). As compared to 10 QL film, the Dirac point shifts ~ 150 meV to lower binding energy. In addition, we performed wider energy scan on 22QL Bi_2Se_3 in order to resolve the bulk bands deeper in the binding energy scale (Figure 4.7 (b)). We can clearly see the dispersion of the several bulk bands. In order to identify these energy bands, we provided EDC at Γ (000) point in Figure 4.7(d). We observed one intense peak (1) located at 1.6 eV, which is the bonding character of Se 4p. Another prominent peak (2) is located at 1.8 eV dominated by Bi 6p bonding orbit. Other two peaks (3 and 4) located

at 2.4 and 3.3 eV binding energy originate from the Bi 6p and Se 4p antibonding orbitals, respectively [18-19].

4.4 Conclusion

In conclusion, we determined the MBE growth parameters that provide high quality Bi_2Se_3 thin films. XRD and LEED patterns show the high crystal quality of the films with sharp diffraction peaks and pattern, respectively. XPS study showed that the stoichiometry of the films is in good agreement of the expected value of 1.5 for Se to Bi atomic ratio. Furthermore, ARPES measurement revealed that Bi_2Se_3 has Dirac like dispersion at and above 6QL. Below 6 QL, the interaction between the surface states located at sample bottom and top opens an energy gap at the Dirac point.

4.5 References

1. H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, *Nature Phys.* 5, 438 (2009).
2. M. Z. Hasan, and C. L. Kane, *Rev. Mod. Phys.* 82, 3045 (2010).
3. T. Valla, Z. H. Pan, D. Gardner, Y. S. Lee, and S. Chu, *Phys. Rev. Lett.* 108, 117601 (2012).
4. T. Schlenk, M. Bianchi, M. Koeini, A. Eich, O. Pietzsch, T. O. Wehling, T. Frauenheim, A. Balatsky, J.-L. Mi, B. B. Iversen et al., *Phys. Rev. Lett.* 110, 126804 (2013).
5. E. Wang, H. Ding, A. V. Fedorov, W. Yao, Z. Li, Y. F. Lv, K. Zhao, L. G. Zhang, Z. J. Xu, J. Schneeloch, R. Zhong, S. H. Ji, L. L. Wang, K. He, X. C. Ma, G. Gu, H. Yao, Q. K. Xue, X. Chen, and S. Y. Zhou, *Nat. Phys.* 9, 621 (2013).
6. T. Yilmaz, I. Pletikosić, A. P. Weber, J. T. Sadowski, G. D. Gu, A. N. Caruso, B. Sinkovic, and T. Valla, *Phys. Rev. Lett.* 113, 067003 (2014).
7. W. Liu, X. Peng, C. Tang, L. Sun, K. Zhang, and J. Zhong, *Phys. Rev. B* 84, 245105 (2011).
8. C.-L. Song, Y.-L. Wang, Y.-P. Jiang, Y. Zhang, C.-Z. Chang, L. Wang, K. He, X. Chen, J.-F. Jia, Y. Wang, Z. Fang, X. Dai, X.-C. Xie, X.-L. Qi, S.-C. Zhang, Q.-K. Xue, and X. Ma, *Appl. Phys. Lett.* 97, 143 118 (2010).
9. B.-L. Young, Z.-Y. Lai, Z. Xu, A. Yang, G. D. Gu, Z.-H. Pan, T. Valla, G. J. Shu, R. Sankar, and F. C. Chou, *Phys. Rev. B* 86, 075137 (2012).
10. Y. Onose, R. Yoshimi, A. Tsukazaki, H. Yuan, T. Hidaka, Y. Iwasa, M. Kawasaki, and Y. Tokura, *Appl. Phys. Express* 4, 083001 (2011).
11. L. He, F. X. Xiu, Y. Wang, A. V. Fedorov, G. Huang, X. F. Kou, M. R. Lang, W. P. Beyermann, J. Zou, and K. L. Wang, *J. Appl. Phys.* 109, 103702 (2011).

12. G. H. Zhang, H. J. Qin, J. Chen, X. Y. He, L. Lu, Y. Q. Li, K. H. Wu, *Adv Funct Mater* 2011, 21, 2351.
13. A. Richardella, D. M. Zhang, J. S. Lee, A. Koser, D. W. Rench, A. L. Yeats, B. B. Buckley, D. D. Awschalom and N. Samarth, *Appl. Phys. Lett.* 97, 262104 (2010).
14. S. E. Harrison, S. Li, Y. Huo, B. Zhou, Y. L. Chen, and J. S. Harris, *Appl. Phys. Lett.* 102(17), 171906 (2013).
15. P. Larson and W. R. L. Lambrecht, *Phys. Rev. B* 78, 195207 (2008).
16. G. Zhang, H. Qin, J. Teng, J. Guo, Q. Guo, X. Dai, Z. Fang, and K. Wu, *Appl. Phys. Lett.* 95, 053114 (2009).
17. H. Zhang, C. X. Liu, X. L. Qi, X. Dai, Z. Fang, and S. C. Zhang, *Nat. Phys.* 5, 438 (2009).
18. V. B. Nascimento, V. E. de Carvalho, R. Paniago, E. A. Soares, L. O. Ladeira, and H. D. Pfannes, *J. Electron Spectrosc. Relat. Phenom.* 104, 99 (1999).
19. T. Takahashi, T. Sagawa, and H. Hamanaka, *J. Non-Cryst. Solids* 65, 261 (1984).

5. Crystal and Electronic Structure of Cr Bulk Doped Bi₂Se₃

5.1 Introduction

In the previous chapter, we introduced the successful growth of topological insulator (TI) Bi₂Se₃ on Al₂O₃ (0001) substrate by molecular beam epitaxial (MBE) method. In this chapter, we focus on the impact of magnetic impurity doping on the electronic structure of a Bi₂Se₃.

TIs have gapless surface states and inverted bulk bands due to the strong spin-orbit interaction. These surface states are protected against to non-magnetic impurities by time reversal symmetry (TRS), which guarantees the Kramers degeneracy at the Dirac point of TIs. On the other hand, net out-of-plane magnetization can break the TRS and lift the Kramers degeneracy. This results in opening a surface energy gap at the Dirac point (Δ_D). Magnetization can be induced in TIs by magnetic impurity doping. This has been theoretically studied [1-3]; and Δ_D was experimentally observed by angle resolved photoemission spectroscopy for various magnetic dopants [4-7].

Such as, one of the early theoretical study from the literature is given in Figure 5.1, which presents the calculated band structures of Co and Cr magnetic impurity doped Bi₂Se₃ [3]. Even though both Cr and Co are magnetic materials, they have different effect on the electronic structure of Bi₂Se₃ in terms of opening Δ_D . Introducing Cr into the system opens 8 meV Δ_D , while the gapless surface state of Bi₂Se₃ is protected against Co doping (Figure 5.1(a-b)). This indicates that Cr doping breaks TRS, while Co doping does not. The different electronic structure of Cr and Co doped Bi₂Se₃ is due to the orientation of the magnetic moments. Bi substitutional (Bi-sub) and Bi interstitial (Bi-int) sites are energetically more favorable for Cr and Co, respectively (Table 5.1). This gives out-of-plane orientation of the magnetic moments for Cr and in-plane orientation of the

magnetic moments for Co (Table 5.1). This concludes that magnetic impurities have to be in the Bi-sub site in order to have out-of-plane magnetization, which breaks the TRS in the bulk doping case. Since Cr satisfies this condition, it is a promising dopant on which Δ_D can be achieved through the broken TRS.

Table 5.1. Formation energies for Cr and Co atoms for different lattice sites, and corresponding magnetic moments (arrows indicate the alignment of magnetic moment) [3].

	Formation energies (eV)		Magnetic moments (μ_B)	
	Cr	Co	Cr	Co
Bi-sub	-0.10	1.69	3.0 $\uparrow$	0.0
Se-sub	3.34	3.44	4.0 $\rightarrow$	1.0 $\rightarrow$
Bi-int	1.14	1.14	4.0 $\rightarrow$	1.5 $\rightarrow$
Se-int	2.09	1.43	0.5 $\rightarrow$	1.5 $\rightarrow$
Bi-ads	1.36	1.3	5.0 $\uparrow$	1.5 $\uparrow$
Se-ads	2.49	1.35	0.4 $\rightarrow$	1.3 $\uparrow$

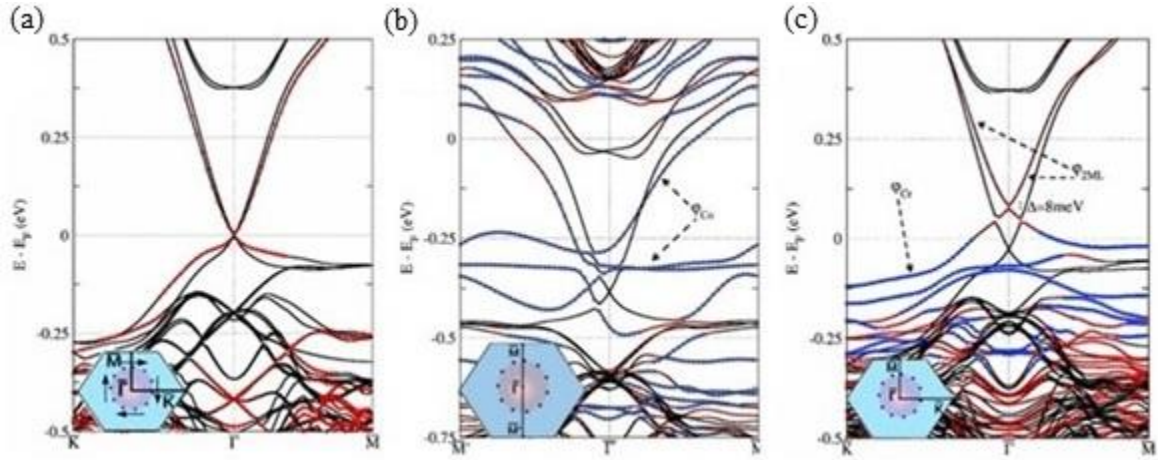


Figure 5.1.(a), (b), (c) are the electronic structure of Bi_2Se_3 , Cr doped Bi_2Se_3 and Co doped Bi_2Se_3 , respectively [3].

In this chapter, we presented combined experiments to investigate the crystal structure, the topological surface state and the magnetic properties of Cr bulk doped Bi_2Se_3 . X-ray diffraction experiment (XRD) was performed to observe changes on the crystal structure of Bi_2Se_3 with Cr doping. Furthermore, we employed angle resolved photoemission spectroscopy (ARPES) in order to investigate the evolution of the topological surface state of Bi_2Se_3 with Cr doping. Core-level experiment was carried out to identify chemical state of Cr. We further extended our investigation by performing the magnetic measurement to study in-plane and out-of-plane magnetic properties of Cr bulk doped Bi_2Se_3 .

5.2 Experiment

High quality of $\text{Bi}_{2-x}\text{Cr}_x\text{Se}_3$ films were grown with molecular beam epitaxy method (MBE) on a Al_2O_3 (0001) substrate. Cr deposition into the bulk of Bi_2Se_3 is achieved by co-deposition of Cr, Bi, and Se. 6N purity Bi and Se was evaporated from resistively heated crucibles and e-beam evaporator was used for Cr source. The films with the thickness of 25 QL were grown at 225 °C substrate temperature. After the growth, the films were kept at 225 °C for additional 10 minutes in order to promote surface crystal quality. Evaporation rates of sources were calibrated with a quartz microbalance sensor. Films Cr concentrations of $x=0.0$, $x=0.05$, 0.1 , 0.16 , 0.22 were synthesized. Stoichiometry of the films was obtained by x-ray photoemission spectroscopy (XPS), which probes near surface region (~ 25 Å). The photoemission studies were done at the University of Connecticut (UCONN) and at the U5UA beam line of the National Synchrotron Light Source (NSLS-I) at the Brookhaven National Laboratory (BNL). He- I_α and Al K_α light sources with SES-100 electron analyzer were used for ARPES and XPS at UCONN, respectively. 52 eV and 104

eV photon energies with Scienta SES-2002 electron analyzer were used to perform ARPES and core-level experiment at the NSLS-I, respectively.

At both laboratories the same growth chamber has been used for sample preparation, which was vacuum inter-locked to the photoemission chambers. Therefore, all experiments were performed without breaking the vacuum. Core-levels binding energies were calibrated with respect to the Fermi level. Bi 5d and Se 3d peaks were fitted with linear combination of Lorentzian and Gaussian line shapes, while Doniach-Sunjic line shape was used for Cr 2p fitting. Shirley type of background was applied to all the core-level spectra. Additionally, XRD crystal structure analysis were performed at the Institute of Material Science (IMS) laboratories at UCONN.

Magnetic characterizations of the samples were done at UCONN by using a superconducting quantum interference device (SQUID) MPMS-5 from Quantum Design. Films were capped with 2nm Se before taking out from the UHV chamber for magnetic measurements. The samples (5 mm $\times$ 5 mm $\times$ 0.5 mm) were mounted on a quartz rod for the parallel magnetic measurements and on a straw for the perpendicular magnetic measurements.

5.3 Results

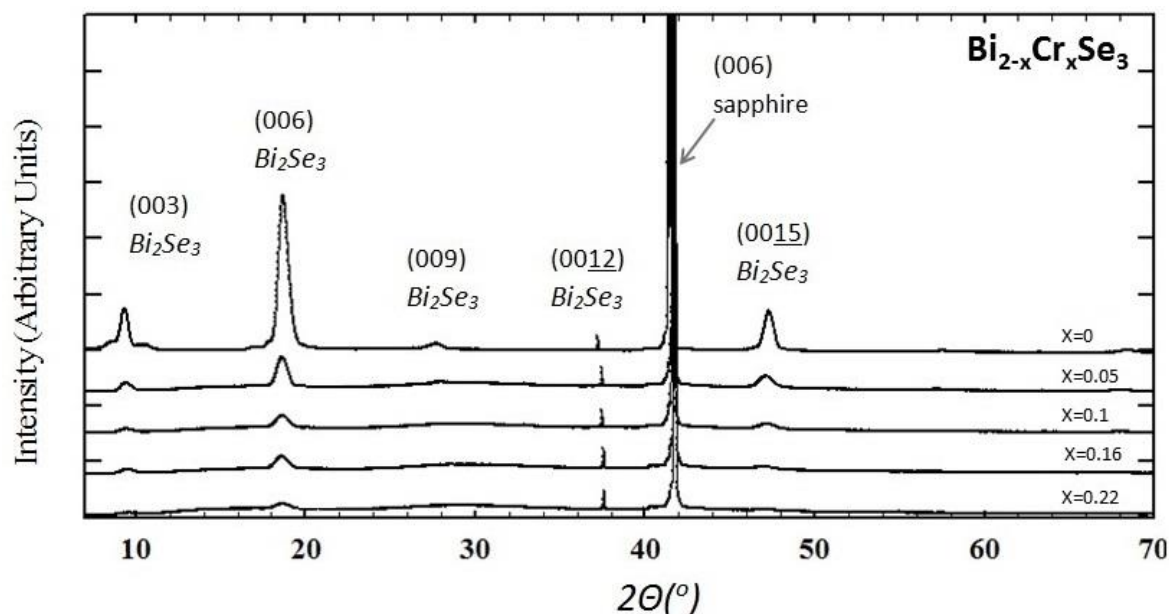


Figure 5.2. XRD patterns for pristine and Cr doped Bi_2Se_3 films. Cr concentrations are written on the right side of the patterns. All the sample have the same thickness of 25 QL. XRD patterns were recorded with Cu x-ray source.

We started our discussion by presenting XRD scans in Figure 5.2 obtained from Cr bulk doped and pristine Bi_2Se_3 films. XRD scans consist of (00 *l*) peaks indicating that the films growth is taking place along the c-axis. The c- lattice parameter is measured to be $28.65 \pm 0.02 \text{ \AA}$ for undoped Bi_2Se_3 , which is consistent with experimental results reported in the literature ($28.636 \text{ \AA}$) [8-9]. The c-lattice parameter stays unchanged with increasing Cr concentration. In addition, (006) peaks of different samples were used to identify rocking curve broadening. Full width at half maximum (FWHM) of (006) peak is measured to be 0.659° for undoped sample and increases with Cr doping reaching 0.982° for highest Cr deposition. This indicates that crystal grain size is getting smaller with increasing Cr concentration.

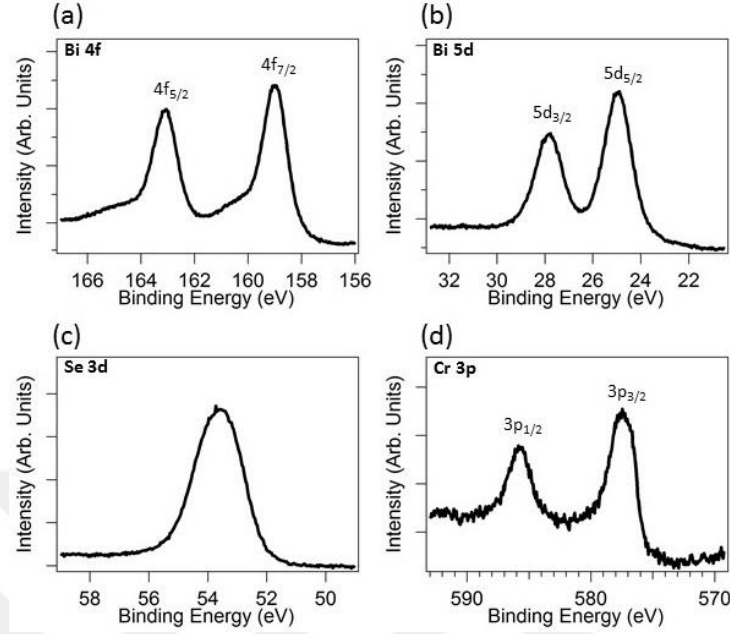


Figure 5.3. Core-level peaks of Bi 4f, Bi 5d, Se 3d and Cr 3p taken from $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$. Spectra were recorded with Al $K\alpha$ x-ray source at the room temperature and at 45° emission angle with SES-100 electron analyzer at UCONN.

As theoretically shown in Reference 3, out-of-plane magnetization can be induced if Cr is in the Bi-sub site (+3 valance state). We performed XPS experiment to identify the valance states of Cr to see if this is the case in our samples. Bi 5d, Bi 4f, Se 3d and Cr 2p core-levels of $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$ are presented in Figure 5.3 and corresponding binding energies are given in Table 5-2, respectively. The binding energies of Cr $2p_{3/2}$ and $2p_{1/2}$ core-levels are measured to be 577.5 eV and 586.0 eV, respectively [Table 5.2]. These binding energies are consistent with the tabulated values in Reference 10 for + 3 valance states of Cr 2p indicating the Cr substituting in Bi-sub site in our samples. Hence, our findings are in line with the theoretical prediction presented in Reference 3.

Table 5.2. Binding Energies (BE) of spectral lines taken from the $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$.

	Bi $f_{7/2}$	Bi $4f_{5/2}$	Bi $5d_{5/2}$	Bi $5d_{3/2}$	Se $3d_{5/2}$	Se $3d_{3/2}$	Cr $2p_{3/2}$	Cr $2p_{1/2}$
BE (eV)	158.8	163.9	25.0	28.1	53.2	54.1	577.5	586.0

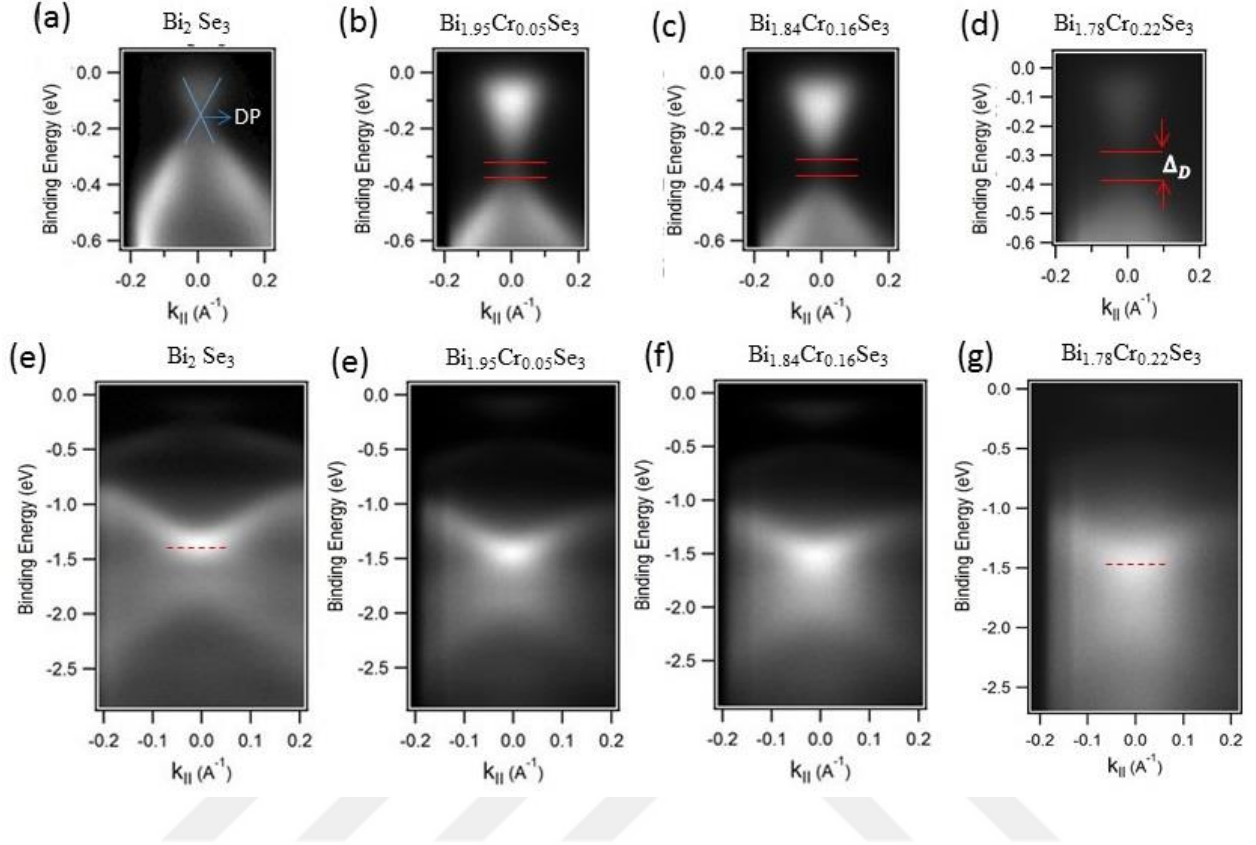


Figure 5.4.(a-d) ARPES 2D intensity plots as a function of energy and momentum from pristine sample and Cr doped samples for $x=0.05, 0.16$ and 0.22 . Solid green line represents the topological surface states and DP stands for the Dirac point. (e-g) Corresponding 2D plots in wider energy range to observe the bulk bands. Δ_D is the energy gap at the Dirac point. Spectra were recorded at the room temperature with 21.2 eV He-I radiation source along the Γ -M direction with SES-100 electron analyzer at UCONN.

An interest in the magnetically doped TIs is to lift the Kramers degeneracy and open Δ_D by breaking the TRS. Δ_D can be examined by performing the ARPES experiment. Here, we presented ARPES measurements performed at UCONN for pristine Bi_2Se_3 ($x=0$) and Cr bulk doped Bi_2Se_3 samples ($x=0.05$ and 0.16) in Figure 5.4(a-d). The distinct energy spectrum of the pristine sample manifests itself as a Dirac point at $\Gamma(000)$ and at the binding energy of 120 meV. Intact and linear dispersions of the surface states marked with solid blue lines in Figure 5.4(a) indicate the gapless and Dirac like dispersion of the surface states in Bi_2Se_3 .

A notable observation in our ARPES measurements is shift of the energy bands to the higher binding energy with Cr doping. The energy shift can be better realized in the bulk band marked with dashed red line in the pristine sample and $x=0.22$ (Figure 5.4(e) and (g)). The binding energy of the band is measured at the highest photoemission intensity point and to be 1.40 meV for the pristine sample and 140 meV for the sample with $x=0.22$ acquiring the total energy shift of 140 meV.

Another pronounced effect of Cr doping on the electronic structure of Bi_2Se_3 is the broadening of the surface states and the bulk bands. The linewidth broadening of the state results in strong overlapping between the energy states that prevents the resolving of the surface states from the bulk bands in samples with $x=0.05$, 0.16 and 0.22 (Figure 5.4(b-d)). Line width broadening of the energy bands is most noticeable at the highest Cr content ($x=0.22$) as seen in the bulk bands (Figure 5.4(g)).

The most remarkable observation in our ARPES measurement is that the relatively small amount ($x=0.05$) of Cr doping into the bulk of Bi_2Se_3 destroys the Dirac-like dispersion and opens Δ_D (Figure 5.4(b)). Increasing the Cr concentration from 0.05 to 0.22 results in larger Δ_D . The size of Δ_D can be estimated from the ARPES measurement represented with the solid red lines as shown in the Figure 5.4. Δ_D is measured to be ~ 50 meV and ~ 100 meV and ~ 130 meV for $x=0.05$, 0.16 and 0.22, respectively. Δ_D observed in our work may originate from broken TRS as long as the ferromagnetic transition temperature (T_c) is above the room temperature.

Literature has reported that ferromagnetism can be only observed below 35 K [10]. However, our ARPES measurements reveal that Δ_D can be observed even at the room temperature, which is far above literature value of T_c (≈ 35 K). Thus, our finding challenges with the literature.

In the explanation of unexpected Δ_D observed in our experiments, other potential origins of Δ_D beside ferromagnetism will be discussed in the conclusion section.

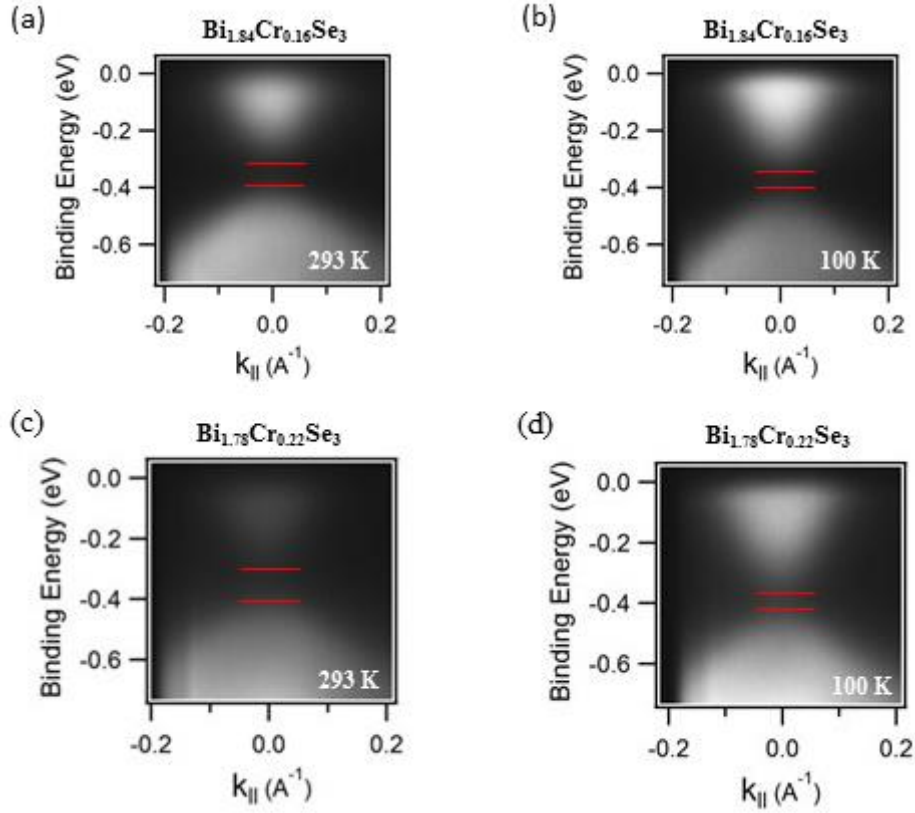


Figure 5.5.(a), (b) ARPES 2D intensity of $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ at the room temperature and at 100 K, respectively. (c), (d) ARPES 2D intensities of $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$ at the room temperature and at 100 K, respectively. Spectra were recorded along the Γ -M direction with He-I light source and SES-100 electron analyzer at UCONN. Red lines indicate the energy gap.

We proceed our experiment by performing the temperature dependent ARPES measurements. The electronic structures of the samples with $x=0.16$ and 0.22 are obtained at the room temperature and at 100 K and given in Figure 5.5. Unexpectedly, Δ_D shows temperature dependence in both samples. Δ_D is measured to be 40 meV for $x=0.16$ and 55 meV for $x=0.22$ at 100 K. The change in Δ_D from the room temperature to 100 K is foreseen when $T_c=35$ K given in the literature is considered. Hence, our observation reveals that Δ_D is not due the ferromagnetism.

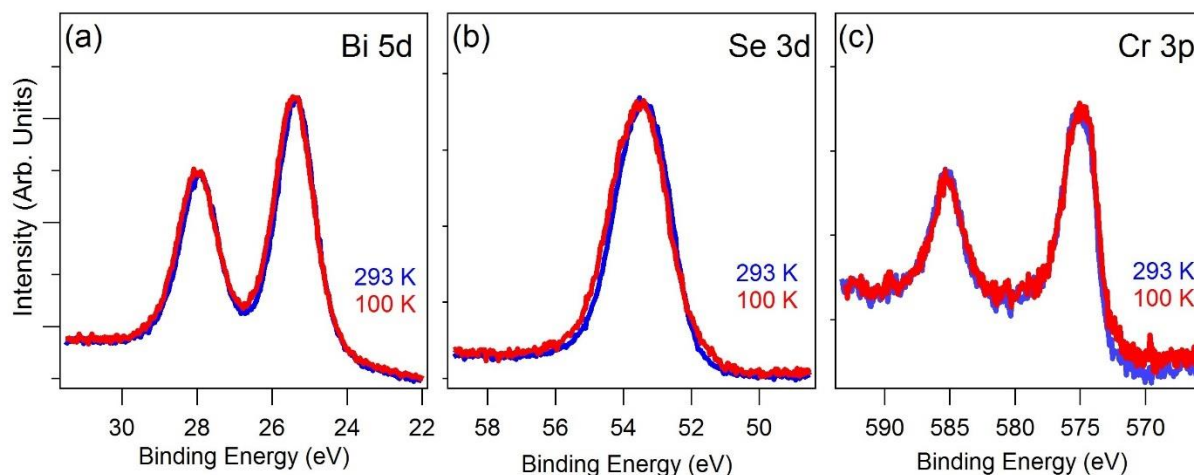


Figure 5.6. Temperature dependent core-level spectra of Bi 5d, Se 3d and Cr 3p obtained from $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$. The data were taken with Al $K\alpha$ x-ray source and SES-100 electron analyzer at UCONN.

Smaller Δ_D at 100 K than the room temperature may originate from the possible changes in the chemical environment with decreasing temperature. We performed XPS at 100 K and at the room temperature on $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$ to see if the chemical environment alters with variable temperature (Figure 5.6). However, core-levels do not show any difference between 100 K and the room temperature except for ~ 60 meV shift to the higher binding energy at 100 K. Hence, the chemical structure of $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$ is stable with temperature showing that change in the chemical environment is not a possible origin of Δ_D .

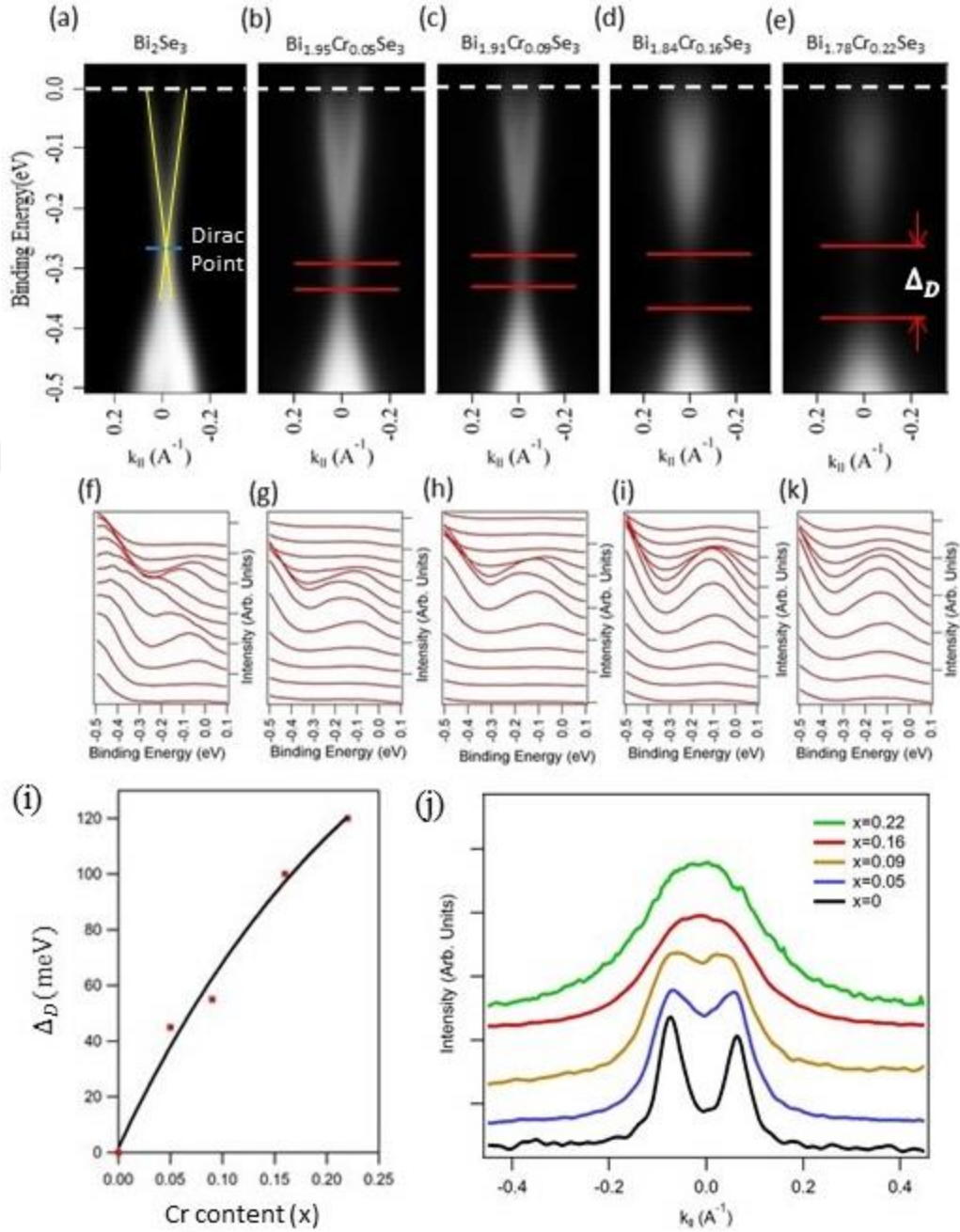


Figure 5.7.(a-e) ARPES 2D intensities along the Γ -M direction for Cr content of $x=0, 0.05, 0.09, 0.16$, and 0.22 . The solid blue line and yellow lines represent the Dirac point (DP) and surface states, respectively in (a). The dashed white lines represent the Fermi level. Spectra were recorded at the room temperature with 52 eV photon energy at NSLS/BNL. (f-k) Corresponding EDC for each ARPES 2D intensity, respectively. (i) Δ_D as a function of Cr content. Solid black line is the fitting. Δ_D is measured based on Reference 10. (j) Momentum dispersive curves (MDCs) at the Fermi level obtained from the ARPES (Cr contents are indicated at the right of MDCs).

Experiments presented so far were done at the surface science laboratory at UCONN. In the ARPES measurements performed at UCONN, the surface states cannot be differentiated from the bulk bands due to overlapping of the energy bands in Cr bulk doped Bi_2Se_3 . One way of the energy mapping of the surface states only in Bi_2Se_3 is to perform ARPES measurement with 52 eV photon energy. The bulk bands in Bi_2Se_3 have vanishing photoionization crosssection for 52 eV resulting in eliminated bulk bands from the ARPES spectra [11-12].

Thus, we performed additional experiments at NSLS/BNL, where variety of the photon energy is available. In Figure 5.7(a-e), ARPES measurements taken from the pristine Bi_2Se_3 sample and Cr doped samples with $x=0.05, 0.09, 0.16, 0.22$ are presented. The ARPES measurements were collected with 52 eV photon energy resulting in the absence of the bulk conduction bands leading to resolve the surface states only as seen in Figure 5.7(a-e).

In the pristine sample (Figure 5.7(a)), the upper and the lower surface states are intact with each other at the Dirac point revealing the gapless nature of the surface states in Bi_2Se_3 . The observations in our ARPES experiments performed at UCONN and at NSLS/BNL are consistent with each other. At the both places, Cr bulk doped Bi_2Se_3 samples show Δ_D in the room temperature ARPES measurements without ferromagnetism.

Another notable observation made from the ARPES measurement taken with 52 eV photon energy is linewidth broadening of the surface states with Cr. In order to observe the schematic broadening of the surface states, the momentum dispersive curves (MDCs) were obtained at the Fermi level and presented in Figure 5.7(j) for different Cr contents. EDC of the pristine sample consists of well resolved two peaks indicating the sharp feature of the surface states. The peaks get prominently broader with increasing Cr content. Linewidth broadening is most noticeable at the Cr contents ($x=0.16$ and 0.22) that two peaks feature in MDC cannot be resolved anymore.

Linewidth broadening of the energy bands can be suppressed by reducing the temperature [11]. Thus, we obtained ARPES 2D intensities at 100 K for the sample with Cr content of $x=0.16$. (Figure 5.8(b)). Unlike our expectation, the surface states even at 100K is not well resolved due to probable inherent linewidth broadening caused by Cr induced crystallinity disorder. In addition, similar to the results obtained at UCONN, the temperature dependent ARPES experiment performed at NSLS/BNL revealed the suppression of Δ_D at low temperature. Δ_D is measured from the bottom of the upper surface state and the top of the lower surface state as indicated with solid red lines in Figure 5.8 and to be 80 meV at 100 K and 120 meV at the room temperature.

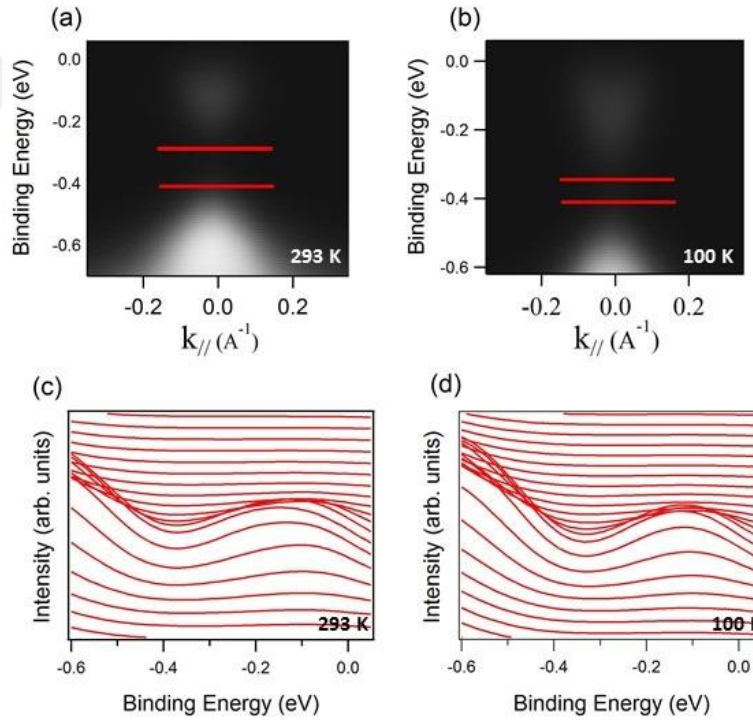


Figure 5.8.(a), (b) Temperature dependent ARPES 2D intensities obtained from $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$ sample the Γ -M direction recorded with 52 eV photon energy at the room temperature and 100 K respectively at NSLS/BNL. (c) and (d) are corresponding EDCs.

The energy resolution of the core-level photoemission spectroscopy setup at UCONN is dominated by 0.85 meV width of Al K_{α} x-ray source, which can be notable eliminated by using the synchrotron radiation. Better energy resolution is needed to resolve possible new peak formation around the main peaks. Thus, we performed core-level experiment on Cr bulk doped samples with 104 eV synchrotron radiation to obtained better resolved core-levels.

Bi 5d and Se 3d core-levels obtained with 104 eV synchrotron radiation at the room temperature are shown in Figure 5.19. The Bi 5d_{5/2} and 5d_{3/2} binding energies were observed to be 25 eV and 28.1 eV, respectively. We can also resolve the spin-orbit splitting on Se 3d peak (Se 3d_{5/2} and 3d_{3/2}) with the binding energies of 53.2 eV and 54.1 eV, respectively. Increasing Cr content leads core-levels to shift towards higher binding energy with maximum energy shift of 200 meV for highest Cr concentration ($x=0.22$). However, we did not observe the formation of any new peaks in the lower or higher binding energy sides of Se 3d and Bi 5d main peaks. Thus, we concluded that Cr doped samples have single phase of Bi_{2-x}Cr_xSe₃.

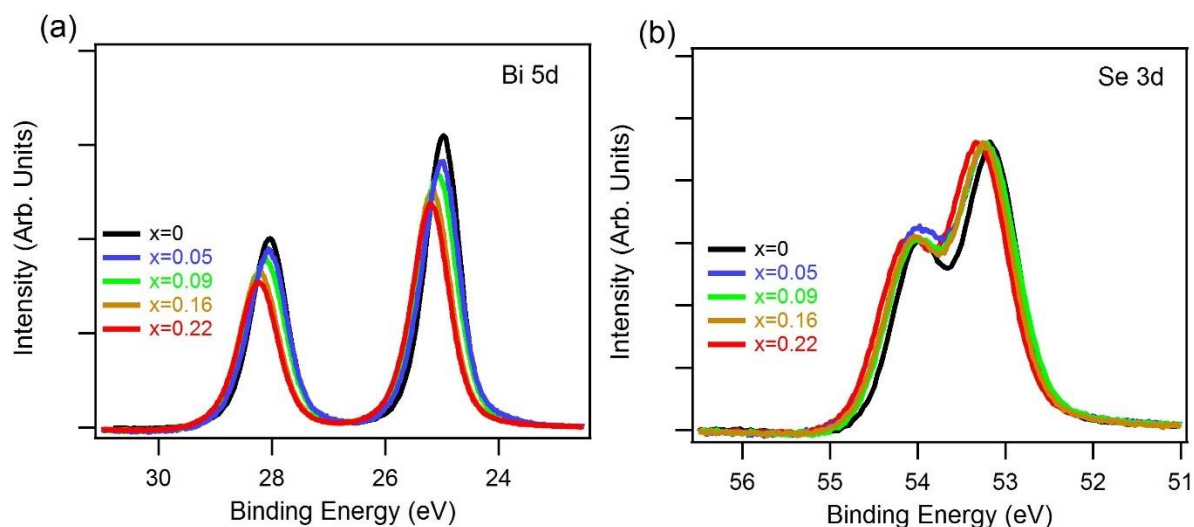


Figure 5.9.(a), (b) High resolution core-level spectra of Bi 5d and Se 3d respectively. Cr concentration is written on the left side of images. Spectra were recorded with 104 eV photon energy at the room temperature at NSLS/BNL.

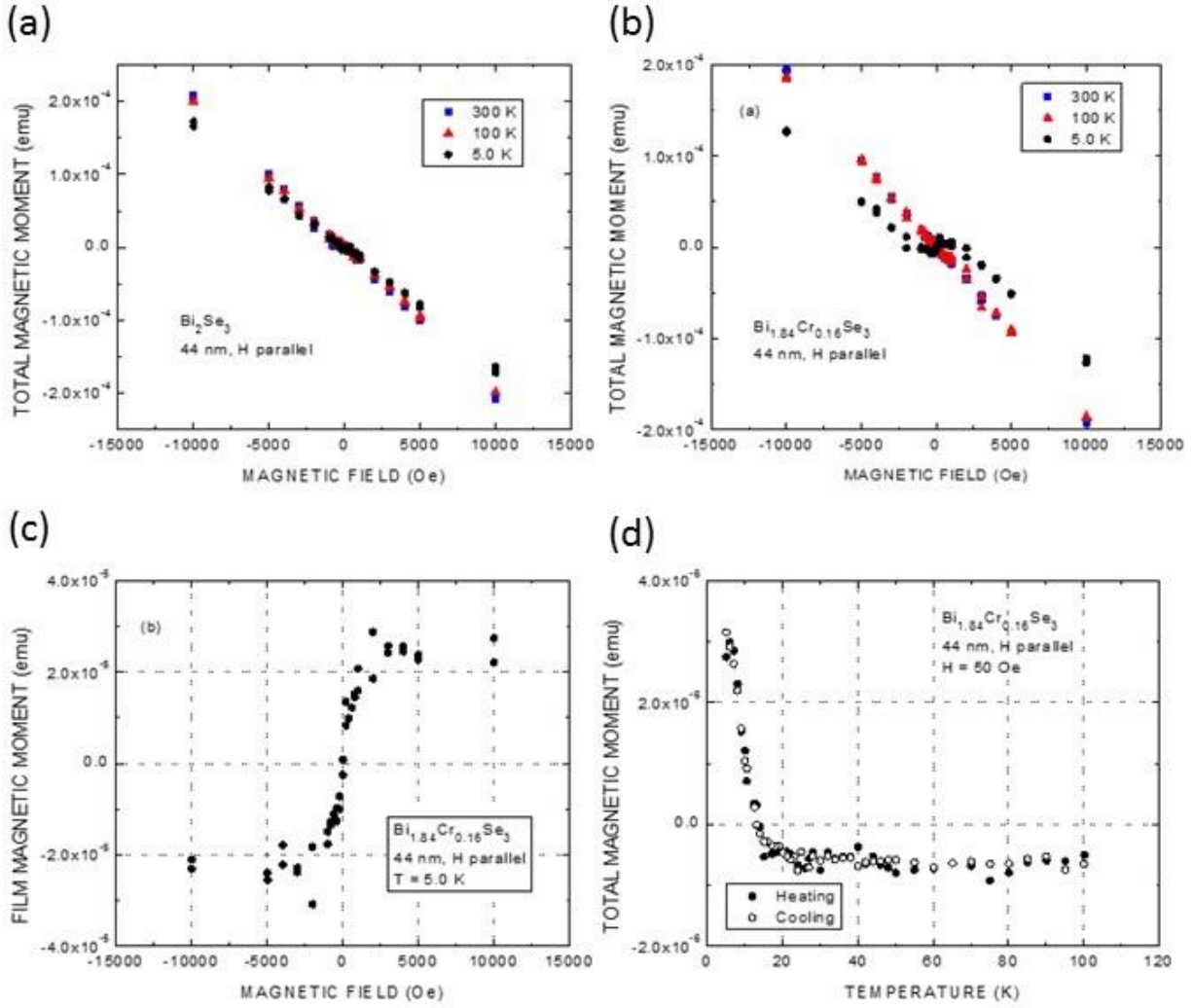


Figure 5.10. (a), (b) In-plane magnetic properties of 46 QL Bi_2Se_3 and $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$. (c) Magnetic hysteresis loop for 46 QL $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ film at 5.0 K after subtracting the diamagnetic background curve obtained at $T = 5.0$ K in (b). (d) Zero-field-cooled/field-cooled curves for 46 QL $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ film in a magnetic field of 50 Oe applied in the sample plane.

So far, we have introduced ARPES 2D intensities of Cr doped Bi_2Se_3 films. Interestingly, Δ_D was observed at the room temperature upon Cr deposition into the bulk of Bi_2Se_3 . This indicates the broken TRS, namely presence of the ferromagnetism at the room temperature. Therefore, we

continue our discussion with characterization of the magnetic properties of Bi_2Se_3 and $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ films for in-plane and out-of-plane orientations.

In Figure 5.10 (a) and (b), total magnetic moment is plotted as a function of in-plane applied magnetic field at $T = 300 \text{ K}$, 100 K , and 5.0 K for the pristine sample and $\text{Bi}_{1.86}\text{Cr}_{0.16}\text{Se}_3$, respectively. In Bi_2Se_3 , magnetic moment is linear through the origin without magnetic hysteresis at the three temperatures, 5 K , 100 K , 300 K , indicating that the sample is diamagnetic. In $\text{Bi}_{1.86}\text{Cr}_{0.16}\text{Se}_3$, magnetic behavior is again linear passing through the origin at 300 K and 100 K ; however, a small, but clear, ferromagnetic component appears for $T = 5.0 \text{ K}$ (Figure 5.10(b)). Magnetic moment per Cr atom is calculated to be $2 \mu_B$ after subtracting diamagnetic contribution of Al_2O_3 substrate from the hysteresis measurement taken at 5 K .

In order to determine the ferromagnetic transition temperature (T_c), the zero-field-cooled/field-cooled (ZFC/FC) magnetization curves was obtained (Figure 5.10(d)). The magnetic response is completely reversible and shows $T_c \approx 10 \text{ K}$.

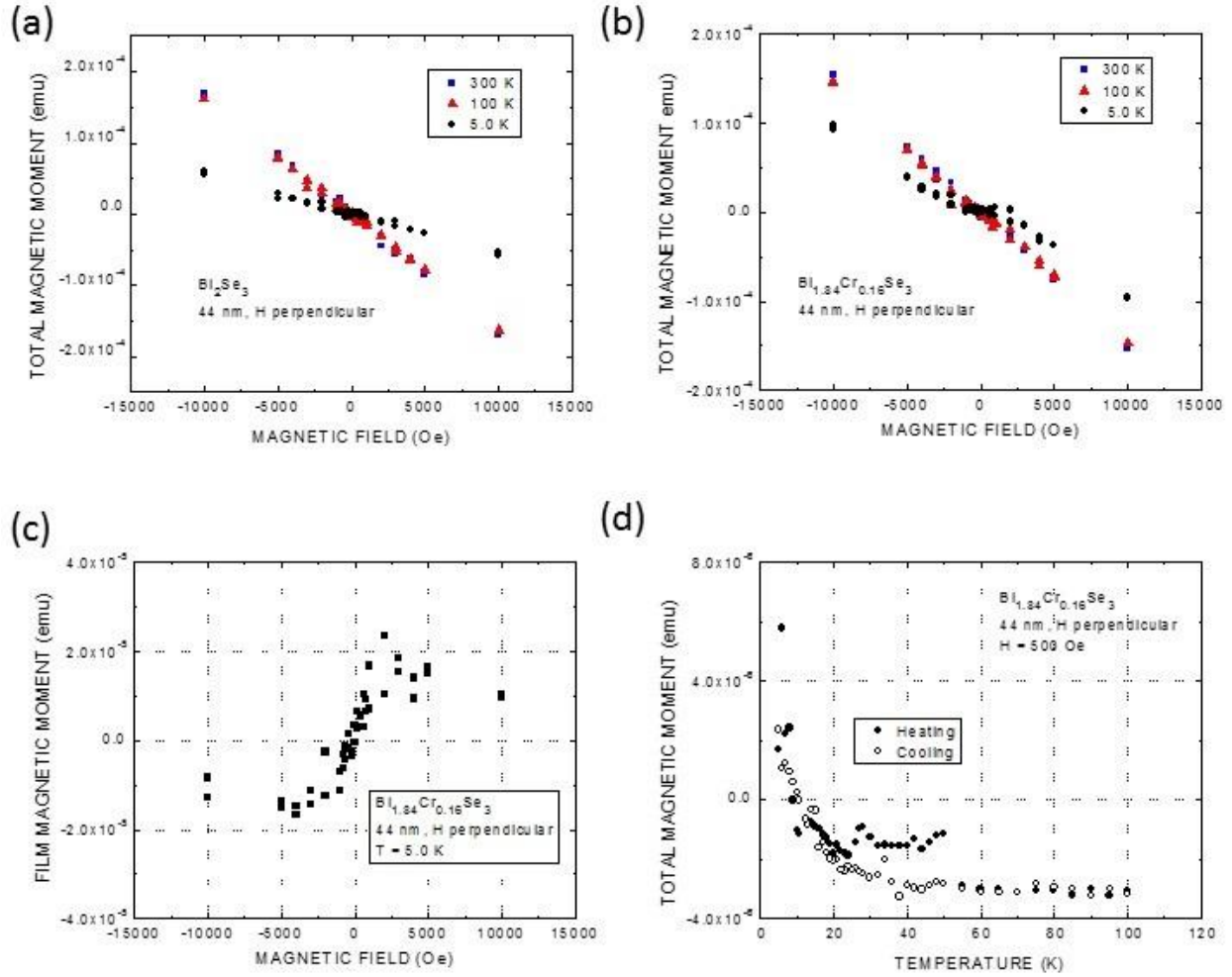


Figure 5.11. (a), (b) Out-of-plane magnetic properties of the 46 QL Bi_2Se_3 and $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$. (c) magnetic hysteresis loop for 46 QL $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ film at 5.0 K after subtracting the diamagnetic background curve obtained at $T = 5.0$ K in (b). (d) Zero-field-cooled/field-cooled curves for 46 QL $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ film in a magnetic field of 500 Oe applied along the sample normal.

We extended our magnetic study to investigate the magnetic properties of Bi_2Se_3 and $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ films for out-of-plane orientations (Figure 5.11). Similar to the in-plane measurements, Bi_2Se_3 does not have a ferromagnetic response as seen linear behavior of total magnetic moment through the origin as a function of applied magnetic field at 300K, 100K and 5K (Figure 5.11 (a)). $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ sample shows the magnetic hysteresis only at 5 K (Figure 5.11 (b)) indicating the presence of ferromagnetism. The value of the magnetic moment per Cr atom is

calculated to be $1.3 \mu_B$ for out-of-plane orientation. This value is obtained from the magnetic hysteresis after diamagnetic contribution of Al_2O_3 substrate is subtracted from the hysteresis measurement taken at 5 K (Figure 5.11 (b)). In addition, zero-field-cooled/field-cooled curves were obtained to determine ferromagnetic transition temperature and it is only $T_c \approx 10$ K for out-of-plane orientation (Figure 1.11(d)).

Interestingly, our magnetic and ARPES challenge with each other. Cr doping into the bulk of Bi_2Se_3 opens Δ_D , which can be resolved even at the room temperature. The origin of the gap is thought to be broken TRS, which is achieved by the out-of-plane ferromagnetism. However, $Bi_{1.84}Cr_{0.16}Se_3$ sample has $T_c \approx 10$ K. Hence, we showed that Δ_D cannot be due to the ferromagnetism as expected.

5.4 Conclusion

In conclusion, we presented detailed photoemission study of Cr bulk doped Bi_2Se_3 . Both the XPS at UCONN and the core-level spectroscopy at NSLS-I indicates the Cr substitution with Bi and absence of any other phase except for $Bi_{2-x}Cr_xSe_3$. The most striking result of our work to observe Δ_D above the $T_c \approx 10$ K. In addition, Δ_D it appears to show temperature dependence with smaller gap size at 100 K compared to the room temperature.

Δ_D can be opened by the broken TRS as a consequence of the out-of-plane magnetization. However, magnetic studies presented in the literature and in our work do not show any sign of ferromagnetism at the room temperature. Therefore, Δ_D at the room temperature challenges researchers to find its origin.

Recently, it was proposed that Cr bulk doping leads to superexchange paramagnetism state with out-of-plane magnetic moment even at the room temperature [13]. This magnetization breaks

TRS and consequently opens Δ_D . On the other hand, magnetic characterizations show the absence of anomalous Hall effect directly indicating that there is no ferromagnetism that can break the TRS [14]. Therefore, this suggests that Δ_D is the result of other physical properties rather than magnetization. TIs are known to be formed by the strong spin-orbit coupling (SOC). The SOC effect has been investigated on various systems. It has shown that quantum phase transition (QPT) from topologically non-trivial insulator to topologically trivial insulator can be induced by weakened SOC [15]. QPT was theoretically shown on $\text{Bi}_{2-x}\text{Fe}_x\text{Se}_3$ with increasing Fe concentration [16]. Weakened SOC is the result of Fe substituting with Bi because Fe has much smaller SOC than Bi. Therefore, the energy gap observed in our samples is likely due to the weakened SOC. Since Cr is much lighter element than Bi, it has much smaller SOC than Bi.

Another possible origin of Δ_D can be the strong resonant scattering suggested by J Sánchez-Barriga and his colleagues for Mn bulk doped Bi_2Se_3 [17]. They showed Mn 3d orbital lies in the vicinity of the Dirac point by calculating the density of states. This results in the localized impurity induced resonance states at and around the Dirac point leading to open Δ_D . They extended their study by performing ARPES measurement for different Mn concentration. They realized that bulk band gap is not changing with doping indicating the absence of QPT. Thus, they conclude that the samples are still topologically non-trivial. Performing the same work presented in their study will be challenging to investigate if this is also the case for Cr doped Bi_2Se_3 .

5.5 References

1. Q. Liu, C.-X. Liu, C. Xu, X.-L. Qi, S.-C. Zhang, Phys. Rev. Lett. 2009, 102, 156603 (2009).
2. R. R. Biswas, A. V. Balatsky, Phys. Rev. B, 81, 233405 (2010).
3. L. B. Abdalla, L. Seixas, T. M. Schmidt, R. H. Miwa, and A. Fazzio, Phys. Rev. B 88, 045312 (2013).

4. B. Hunt, J. D. Sanchez-Yamagishi, A. F. Young, M. Yankowitz, B. J. LeRoy, K. Watanabe, T. Taniguchi, P. Moon, M. Koshino, P. Jarillo-Herrero, and R. C. Ashoori, *Science* 340, 1427 (2013).
5. Y. L. Chen, J. H. Chu, J. G. Analytis, Z. K. Liu, K. Igarashi, H. H. Kuo, X. L. Qi, S. K. Mo, R. G. Moore, D. H. Lu, M. Hashimoto, T. Sasagawa, S. C. Zhang, I. R. Fisher, Z. Hussain, Z. X. Shen, *Science*, 329, 659 (2010).
6. S.Y. Xu, M. Neupane, C. Liu, D. Zhang, A. Richardella, L. A. Wray, N. Alidoust, M. Leandersson, T. Balasubramanian, J. Sánchez-Barriga, O. Rader, L. Gabriel, S. Bartosz, J. H. Dil, J. Osterwalder, T. R. Chang, H. T. Jeng, H. Lin, A. Bansil, N. Samarth, M. Z. Hasan, *Nat. Phys.* 2012, 8, 616–622
7. L. A. Wray, S. Y. Xu, Y. Xia, D. Hsieh, A. V. Fedorov, Y. S. Hor, R. J. Cava, A. Bansil, H. Lin, and M. Z. Hasan, *Nature Phys.* 7, 32 (2010).
8. L. J. Collins-McIntyre, S. E. Harrison, P. Schönherr, N.-J. Steinke, C. J. Kinane, T. R. Charlton, D. Alba-Venero, A. Pushp, A. J. Kellock, S. S. P. Parkin, J. S. Harris, S. Langridge, G. van der Laan, and T. Hesjedal, *Eur. Phys. Lett.* 107, 57009 (2014).
9. H. Cao, S. Xu, I. Miotkowski, J. Tian, D. Pandey, M. Z. Hasan, and Y. P. Chen, *Phys. Status Solidi RRL* 7, 133 (2013).
10. X. F. Kou, W. J. Jiang, M. R. Lang, F. X. Xiu, L. He, Y. Wang, Y. Wang, X. X. Yu, A. V. Fedorov, P. Zhang, and K. L. Wang, *J. Appl. Phys.* 112, 063912 (2012).
11. Z.-H. Pan, A. V. Fedorov, D. Gardner, Y. S. Lee, S. Chu, and T. Valla, *Phys. Rev. Lett.* 108, 187001 (2012).
12. E. Wang, H. Ding, A. V. Fedorov, W. Yao, Z. Li, Y. F. Lv, K. Zhao, L. G. Zhang, Z. J. Xu, J. Schneeloch, R. Zhong, S. H. Ji, L. L. Wang, K. He, X. C. Ma, G. Gu, H. Yao, Q. K. Xue, X. Chen, and S. Y. Zhou, *Nat. Phys.* 9, 621 (2013).
13. C.-Z. Chang, P. Tang, Y.-L. Wang, X. Feng, K. Li, Z. Zhang, Y. Wang, L.-L. Wang, X. Chen, C. Liu, W. Duan, K. He, X.-C. Ma, and Q.-K. Xue, *Phys. Rev. Lett.* 112, 056801 (2014).
14. J. Zhang, C.-Z. Chang, P. Tang, Z. Zhang, X. Feng, K. Li, L.-L. Wang, X. Chen, C. Liu, W. Duan, K. He, Q.-K. Xue, X. Ma, and Y. Wang, *Science* 339, 1582 (2013).
15. J. Liu and D. Vanderbilt, *Phys. Rev. B* 88, 224202 (2013).
16. H. Jin, J. Im, and A. J. Freeman, *Phys. Rev. B* 84, 134408 (2011).
17. J. Sánchez-Barriga, A. Varykhalov, G. Springholz, H. Steiner, R. Kirchschrager, G. Bauer, O. Caha, E. Schierle, E. Weschke, A. A. Ünal, S. Valencia, M. Dunst, J. Braun, H. Ebert, J. Minár, E. Golias, L. V. Yashina, A. Ney, V. Holý and O. Rader, *Nat Commun* 7 (2016).

6. Impact of Cr Surface Deposition on the Chemical Environment and the Electronic Structure of Bi_2Se_3

6.1 Introduction

Interaction between the magnetic impurities and the topological surface states is under heavy interest [1-3]. Because magnetization can break the time reversal symmetry (TRS) and open an energy gap at the Dirac point of topological insulators (TIs) [4-9]. Magnetization can be induced in TIs by the deposition of magnetic impurities into the bulk as presented in the previous chapter for Cr bulk doped Bi_2Se_3 , which opens an energy gap at the Dirac point without any magnetic response. In this chapter, we study the topological surface states of Bi_2Se_3 under the different approach of impurity deposition, which is the introducing magnetic impurities on the surface rather than into the bulk of Bi_2Se_3 .

In the surface deposition method, ferromagnetism can be induced by the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction if the Dirac point is close to the Fermi level [7, 10-12]. In RKKY interaction ferromagnetism originates from the coupling between localized core spins and conduction electrons in a metal. Ferromagnetism induced by RKKY interaction is expected to be stronger than the bulk ferromagnetism in TIs because it is inversely proportional to the energy gap [7]. Therefore, introducing magnetic impurities on the surface of TIs is expected to break TRS through the RKKY interaction and open an energy gap at Dirac point.

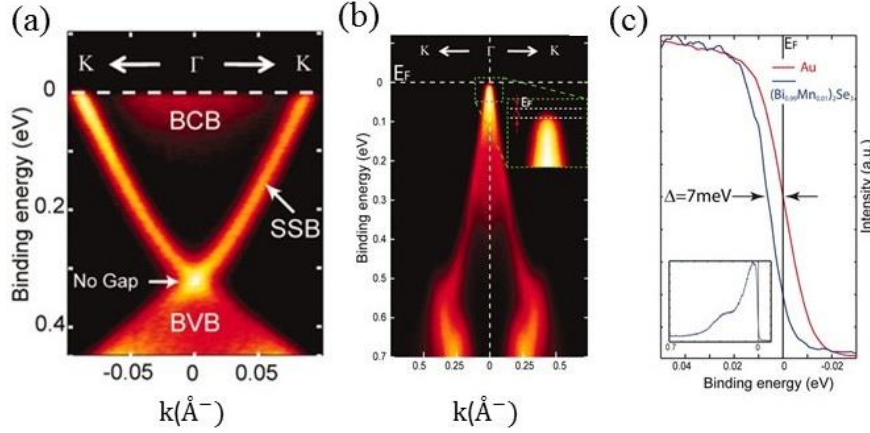


Figure 6.1. (a) ARPES 2D intensity of Bi_2Se_3 . BCB, BVB and SSB represent bulk conduction band, bulk valence band and surface state band, respectively. (b) ARPES 2D intensity of $(\text{Bi}_{0.99}\text{Mn}_{0.01})_2\text{Se}_3$ shows the Fermi level inside the surface Dirac gap. Inset: close-up of the dispersion in the vicinity of the Fermi level. (c) The energy dispersive curve (EDC) along the white dashed line in (b) and taken from the Au reference showing 7 meV energy gap. Spectra were recorded at 10 K with 48 eV photon energy [7].

In the literature, the gap opening by RKKY interaction was investigated on Mn doped Bi_2Se_3 by angle resolved photoemission spectroscopy (ARPES) technique as shown in Figure 6.1 [7]. The pristine sample shows Dirac like energy dispersion with the Dirac point located at ~300 meV. Upon Mn doping, the Dirac point shifts to the Fermi level and an energy gap merges at the Dirac point as seen in Figure 6.1(b). This is also confirmed by the energy dispersive curves (EDCs) taken at the $\Gamma(000)$ point of Mn doped Bi_2Se_3 and Au reference (Figure 6.1(c)). This is seen as the leading edge of the sample is located 7 meV below the Fermi level of Au reference. This indicates that the gap opening at the Dirac point is due to the RKKY interaction induced ferromagnetism.

Here, we investigate the electronic structure and chemical environment of Bi_2Se_3 upon Cr surface deposition in order to search for the possible gap opening at the Dirac point through RKKY interaction. We performed angle resolved photoemission spectroscopy (ARPES) to evaluate Dirac surface state, and core-level spectroscopy of Bi 5d, Se 3d and Cr 3p to identify chemical states of

the elements. We continue our discussion by giving the experimental techniques and procedures in the next section.

6.2 Experiment

High quality of Bi_2Se_3 films were grown with molecular beam epitaxial method on Al_2O_3 (0001) substrate by evaporating high purity Bi (99.9999%) and Se (99.9999%) from resistively heated crucibles. Two-step growth method was applied by first growing 2 quintuple layer (QL) of Bi_2Se_3 at 390 K, and additional 23 QL of Bi_2Se_3 film was deposited at 465 K. After the growth, films were kept at 465 K for 10 minutes in order to promote surface crystal quality. Cr is deposited on the surface of Bi_2Se_3 at the room temperature by using e-beam evaporator. Evaporation rates of sources were calibrated with quartz microbalance sensor. Growth chamber was attached to experimental chamber with base pressure of 2×10^{-11} torr at U5UA beam line of National Light Source (NSLS) at the Brookhaven National Laboratory (BNL). Therefore, experiments were performed without breaking the vacuum hence, in-situ without any post-growth surface contamination. ARPES and core-level spectroscopy were carried out with 52 eV and 104 eV synchrotron radiations, respectively with Scienta SES-2002 electron analyzer with 10 meV energy and 0.15° angular resolution. Core-levels binding energies were calibrated with respect to the Fermi level with the ± 0.02 eV precision. Bi 5d and Se 3d peaks were fitted with linear combination of Lorentzian and Gaussian line shapes, while Doniach-Sunjić line shape was used for Cr 3p fitting. Shirley type of background was applied to all the core-levels.

6.3 Results

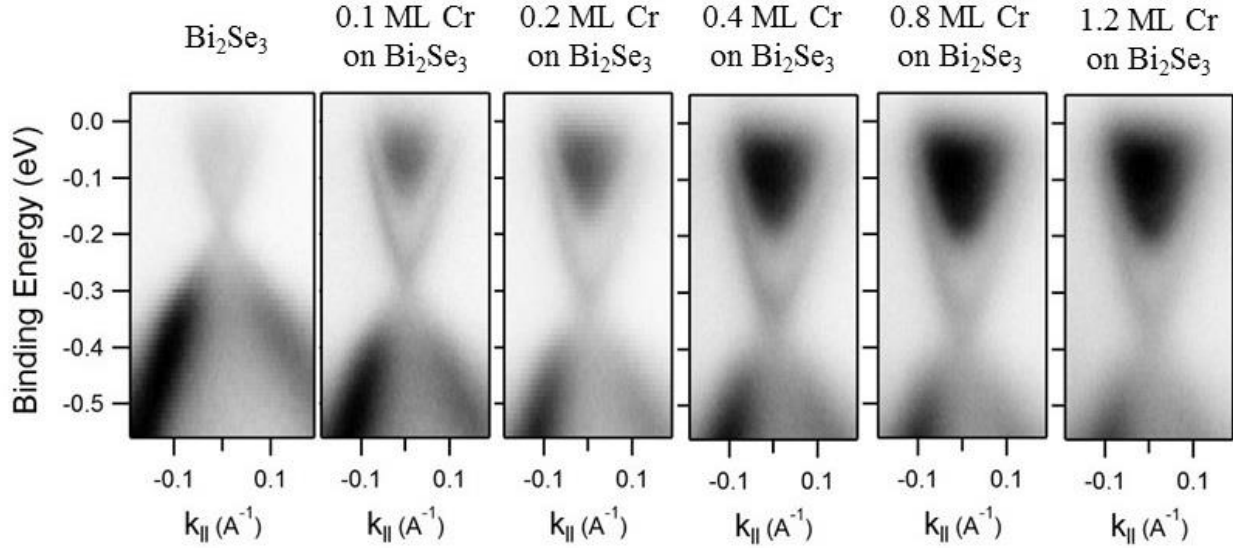


Figure 6.2. ARPES 2D photoemission intensity plots as a function of energy and momentum from pristine sample and Cr deposited on the surface of Bi_2Se_3 . Spectra were recorded at the room temperature with 21.2 eV He-I radiation source at UCONN with SES-100 electron analyzer. $k_{\parallel}$ direction is along the Γ -M direction.

Figure 6.2 shows the evolution of the topological surface states (TSSs) of Bi_2Se_3 under the room temperature Cr deposition on the surface. Clean Bi_2Se_3 shows clear Dirac like dispersion with Dirac point located at $\Gamma(000)$ and at 190 meV binding energy. Deposition of 0.1 monolayer (ML) Cr on the surface of Bi_2Se_3 leads the Dirac point to shift higher binding energy. Increasing the Cr deposition thickness results in further shift of the Dirac point to higher binding energy and the Dirac point is located at 375 meV binding energy for 1.2 ML Cr deposition. Unlike the bulk doping of Cr, ARPES measurements taken at the room temperature do not show gap opening at the Dirac point.

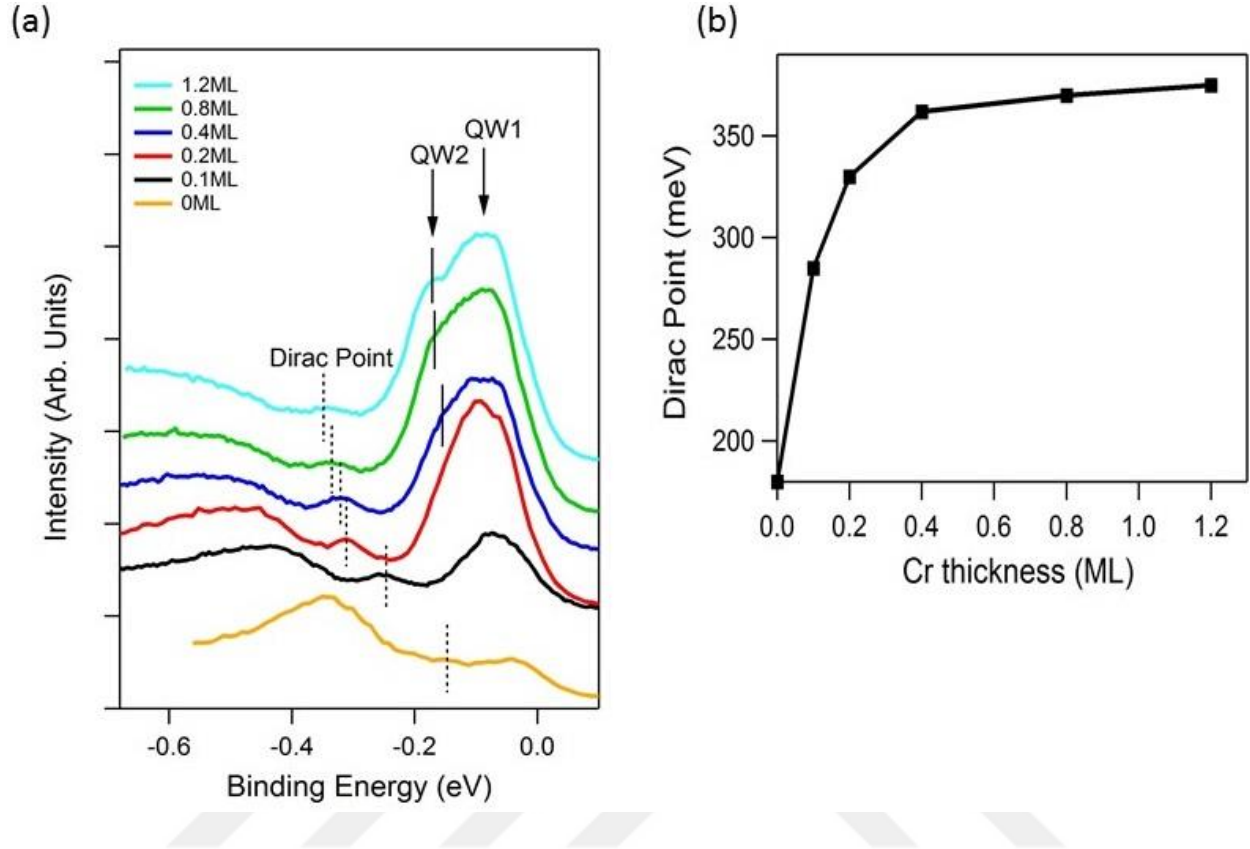


Figure 6.3.(a) EDC at $\Gamma(000)$ for different thickness of the Cr on the surface of Bi_2Se_3 . Dashed black lines represent the binding energy of the Dirac Point. Two quantum well states are attributed as QW1 and QW2. (b) Binding energy of the Dirac point as a function of Cr thickness in monolayer (ML). EDCs are obtained from the ARPES measurements presented in Figure 6.2.

For further investigation of the development of the electronic structure upon Cr surface deposition on Bi_2Se_3 , we presented EDCs at $\Gamma(000)$ in Figure 6.3(a). The binding energy of the Dirac point is represented with the dashed black lines and it is given as a function of the Cr thicknesses in Figure 6.3(b). Binding energy of the Dirac point increases with Cr thickness up to 0.4 ML, and it shows almost linear behavior for further deposition of Cr. Furthermore, increasing Cr thickness results in the observation of new energy bands located at 85 meV and 165 meV indicated by QW1 and QW2 in Figure 6.3(a) for 1.2 ML Cr. These states are the quantum well states formed by the confinement of electrons perpendicular to sample surface [13].

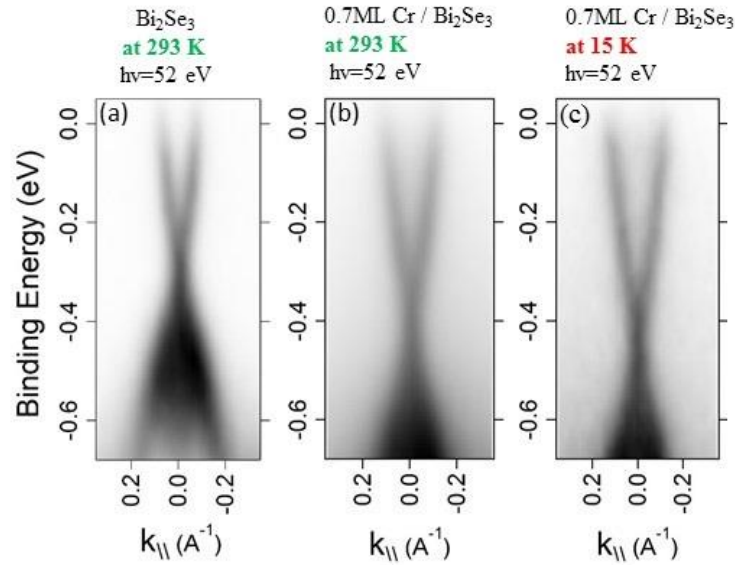


Figure 6.4. (a), (b) ARPES 2D intensities of pristine and 0.7 ML Cr surface doped sample at the room temperature. (c) ARPES 2D intensity of 0.7 ML Cr surface doped sample at 15 K. Spectra were recorded with 52 eV photon energy along the Γ -M direction at NSLS/BNL.

In addition to ARPES measurements done at the surface science laboratory at UCONN, we conducted additional experiment at NSLS/BNL to obtain high resolution photoemission study. At NSLS/BNL, experiments were done with larger electron analyzer and synchrotron radiation, which increases the total energy resolution of the photoemission experiments. Another advantage of this facility is availability of different photon energies. We can choose such photon energy in order to only tune the TSS and eliminate bulk bands from the ARPES measurement. It can be found in the literature that ARPES measurements performed with 52 eV photon energy consists of only the surface states of Bi_2Se_3 without bulk bands [14]. Therefore, we continue our discussion by presenting ARPES measurements with 52 eV photon energy.

ARPES measurements obtained at NSLS/BNL from the pristine sample and 0.7 ML Cr deposited Bi_2Se_3 are shown in Figure 6.4. Pristine film (Figure 6.4 (a)) shows clear Dirac like dispersion with Dirac point located at $\Gamma(000)$ and at 280 meV binding energy. Upon the deposition of 0.7 ML Cr on the surface of Bi_2Se_3 , Dirac point shifts to higher binding energy around 135 meV. ARPES measurements performed at UCONN does not show an energy gap opening at the Dirac point at the room temperature. This could be due to the low ferromagnetic transition temperature. Therefore, electronic structure is also recorded at 15 K in the vicinity of Dirac point. Once sample is cooled, Dirac point has additional 40 meV shift to higher binding energy. Furthermore, an energy gap is expected to open at the Dirac point due to magnetic impurity doping, which can induce long range ferromagnetism. On the other hand, our ARPES measurement at 15 K shows no evidence of an energy gap opening at Dirac point (Figure 6.4(c)).

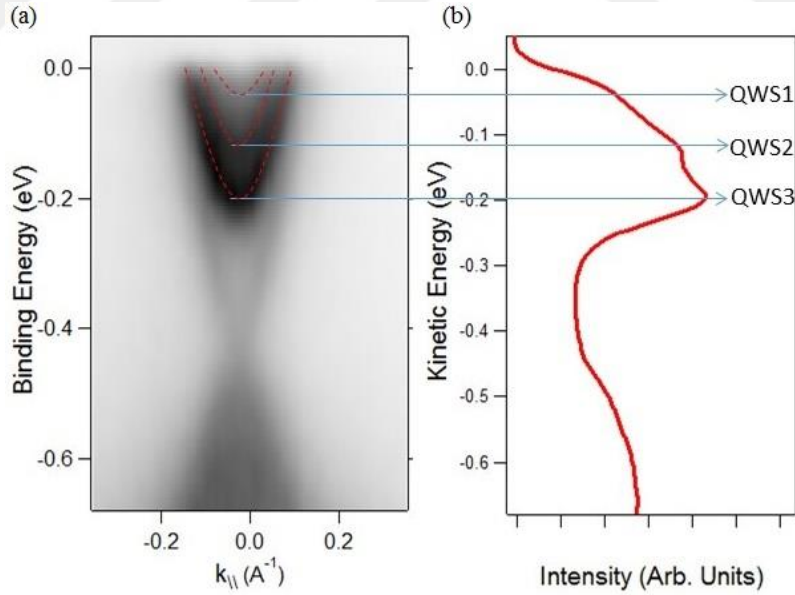


Figure 6.5. (a) ARPES 2D intensity of 0.7 ML Cr surface doped Bi_2Se_3 at 15 K with 21.2 eV photon energy along the Γ -M direction. (b) EDC at $\Gamma(000)$ point. Dashed red lines represents the QWS.

In order to resolve the bulk bands, we presented ARPES 2D intensity of 0.7 ML Cr doped Bi_2Se_3 taken with 21.2 eV photon energy at 15 K. Since the experimental resolution is improved

by the larger electron analyzer and synchrotron radiation, we are able to distinguish three QWSs (QWS1, QWS2, QWS3). These states are indicated with dashed red lines in Figure 6.5.

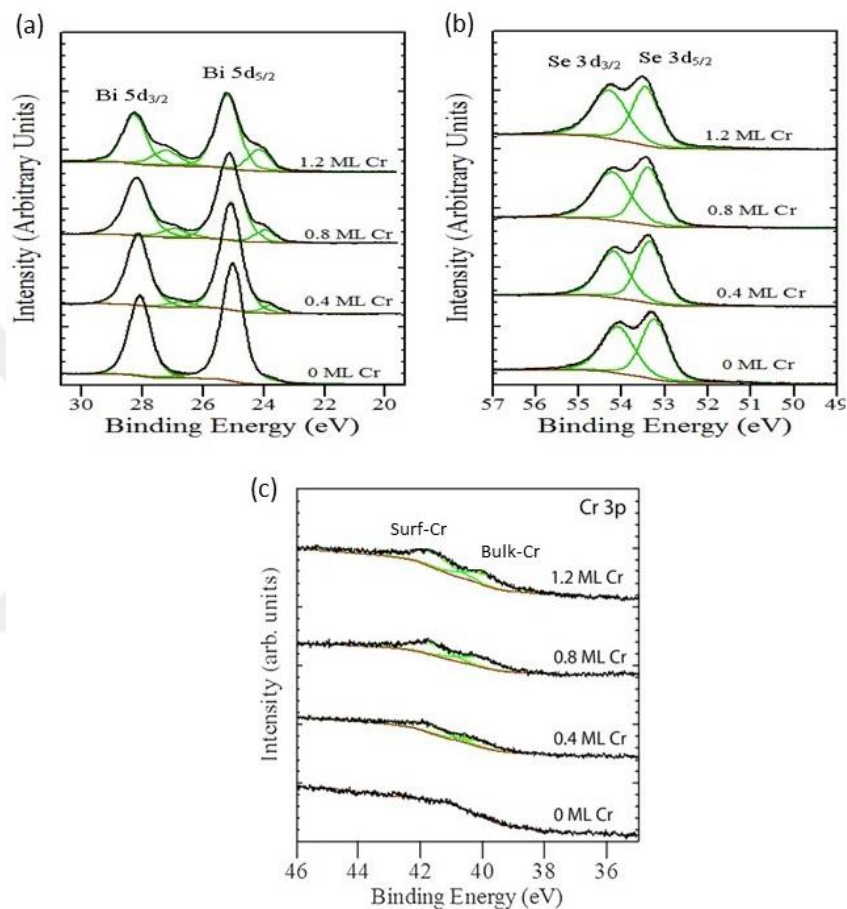


Figure 6.6. Core spectra of Bi 5d, Se 3d and Cr 3p as a function of Cr coverage levels are given in (a), (b) and (c) respectively. Thick green lines represent the linear combination of Lorentzian and Gaussian fitting line shape, and thick brown line is Shirley type of background. Cr amount is written on the right sides of spectra. Core-levels recorded at the room temperature with 104 eV photon energy at NSLS/BNL.

In order to study the impact of the Cr deposition on the chemical environment of Bi₂Se₃, we performed core-level photoemission spectroscopy as a function of Cr thickness on the surface of Bi₂Se₃ (Figure 6.6). Bi 5d_{5/2} and 5d_{3/2} binding energies were measured to be 25 eV and 28 eV, respectively for undoped sample (Figure 6.6(a)). Cr deposition leads to formation of new

structures in the lower binding energy sides of Bi 5d_{5/2} and 5d_{3/2} main peaks. These new peaks are located at 23.9 eV and 26.9 eV binding energies, which correspond to the binding energy of Bi metal [15]. Observation of such shoulders indicates that Cr atoms diffuse into sub-layers and substitute with Bi resulting in the formation of Bi metal. The Se 3d_{5/2} and 3d_{3/2} binding energies for clean film are 53.4 eV and 54.2 eV, respectively (Figure 6.6(b)). Upon Cr deposition, we did not observe prominent broadening of full width at half maximum (FWHM) of Se 3d peaks or the formation of chemically different peaks or shoulders as in the case of Bi. This suggests the absence of intercalated or Cr-substituted Se. Bi 5d and Se 3d peaks show 200 meV shift towards higher binding energy, which is an expected result of electron doping character of Cr deposition on the surface (Figure 6.6(c)). Cr 3p photoemission peak is hardly resolved at lowest Cr deposition due to its diffusion into film. Interestingly, Cr 3p can be observed as a doublet with the deposition amount of Cr increases. This can be explained by the formation of Bi metal peak and shift of core-levels to higher binding energy. Binding energy shifts of Bi 5d and Se 3d core-levels indicate electron doping of the system, which proves the presence of Cr ad-atoms on the surface. On the other hand, the production of Bi metal indicates existence of Bulk-Cr. Therefore, we attribute two Cr 3p peaks to surface-Cr (Sur-Cr) and substituted -Cr (Bulk-Cr), which are located at 41.9 eV and 40.4 eV binding energies, respectively. We observed that increasing Cr coverage level leads to an enhancement of both 3p peak intensities. This agrees with the observation of increasing Bi 5d shoulder intensity and the shift of Bi 5d and Se 3d peaks to higher binding energy with Cr deposition. We should point out that the double peak structure observed in Cr 3p spectra is not due to the spin-orbit splitting between Cr 3p_{3/2} and Cr 3p_{1/2} because spin-orbit splitting energy in these peaks is negligible, and the peaks are located at 42.2 eV binding energy [15].

Similar results can be found in the literature for different impurity deposition on the surface of TIs [16-18]. For example, recent study presented in Reference 17 showed that Fe deposition on the surface of Bi_2Se_3 also gives rise to form chemically different Bi similar to our case.

6.4 Conclusion

We demonstrated schematic study on the evolution of chemical environment and surface states of Bi_2Se_3 under Cr surface deposition. We observed the formation of new structure in the lower binding energy sides of the Bi 5d, while such formation is absent in Se 3d. Binding energy of the shoulder corresponds to binding energy of the Bi metal indicating the Cr substitution with Bi. This argument is supported by Cr 3p peak as well as by the observation of two distinct Cr 2p peaks.

Remarkably, surface deposition of Cr does not open an energy gap at the Dirac point, unlike the expectations and in contrast to our Cr bulk doped samples. There could be several reasons of protected gapless surface state under the Cr surface deposition. One simple explanation is in-plane orientation of the magnetic moments, which cannot break the TRS. Another possible reason is shift of Dirac points to the higher binding energy with each Cr deposition. This can prevent the formation of long range ferromagnetism by RKKN interaction [7]. Another suggestion is that the impurity resonance states contribute to the spectral weight around the Dirac point, which can rapidly fill the energy gap at the Dirac point [19]. In this model, energy gap at the Dirac point is present at low impurity potential. Increasing the impurity potential causes an energy shift of the Dirac point to the lower binding energy and it results in filling the energy gap at the Dirac point by the impurity states. However, in the Cr surface doped case, the Dirac point is shifting to the higher binding energy in contrast to this model. Therefore, it is more favorable that gapless surface

state is protected against to Cr surface deposition because of the absence of ferromagnetism, which is not developed by the RKKY interaction due to the high binding energy of the Dirac point.

6.5 References

1. Q. Liu, C.-X. Liu, C. Xu, X.-L. Qi, S.-C. Zhang, *Phys. Rev. Lett.*, 102, 156603 (2009).
2. R. R. Biswas, A. V. Balatsky, *Phys. Rev. B*, 81, 233405 (2010).
3. L. B. Abdalla, L. Seixas, T. M. Schmidt, R. H. Miwa, and A. Fazzio, *Phys. Rev. B* 88, 045312 (2013).
4. M. Scholz, J. Sanchez-Barriga, D. Marchenko, A. Varykhalov, A. Volykhov, L. Yashina, and O. Rader, preceding Letter, *Phys. Rev. Lett.* 108, 256810 (2012).
5. T. Schlenk, M. Bianchi, M. Koleini, A. Eich, O. Pietzsch, T. O. Wehling, T. Frauenheim, A. Balatsky, J.-L. Mi, B. B. Iversen, J. Wiebe, A. A. Khajetoorians, Ph. Hofmann, and R. Wiesendanger, *Phys. Rev. Lett.* 110, 126804 (2013).
6. B. Hunt, J. D. Sanchez-Yamagishi, A. F. Young, M. Yankowitz, B. J. LeRoy, K. Watanabe, T. Taniguchi, P. Moon, M. Koshino, P. Jarillo-Herrero, and R. C. Ashoori, *Science* 340, 1427 (2013).
7. Y. L. Chen, J. H. Chu, J. G. Analytis, Z. K. Liu, K. Igarashi, H.-H. Kuo, X. L. Qi, S. K. Mo, R. G. Moore, D. H. Lu, M. Hashimoto, T. Sasagawa, S. C. Zhang, I. R. Fisher, Z. Hussain, Z. X. Shen, *Science*, 329, 659 (2010).
8. S.-Y. Xu, M. Neupane, C. Liu, D. Zhang, A. Richardella, L. A. Wray, N. Alidoust, M. Leandersson, T. Balasubramanian, J. Sánchez-Barriga, O. Rader, L. Gabriel, S. Bartosz, J. H. Dil, J. Osterwalder, T.-R. Chang, H.-T. Jeng, H. Lin, A. Bansil, N. Samarth, M. Z. Hasan, *Nat. Phys.*, 8, 616–622 (2012).
9. L. A. Wray, S. Y. Xu, Y. Xia, D. Hsieh, A. V. Fedorov, Y. S. Hor, R. J. Cava, A. Bansil, H. Lin, and M. Z. Hasan, *Nature Phys.* 7, 32 (2010).
10. K. He, X.-C. Ma, X. Chen, L. Lu, Y.-Y. Wang, and Q.-K. Xue, *Chin. Phys. B* 22, 067305 (2013).
11. Q. Liu, C.-X. Liu, C. Xu, X.-L. Qi, and S.-C. Zhang, *Phys. Rev. Lett.* 102, 156603 (2009).
12. D. A. Abanin and D. A. Pesin, *Phys. Rev. Lett.* 106, 136802 (2011).
13. Y. Zhang et al., *Nature Phys.* 6, 584 (2010).
14. E. Wang, H. Ding, A. V. Fedorov, W. Yao, Z. Li, Y. F. Lv, K. Zhao, L. G. Zhang, Z. J. Xu, J. Schneeloch, R. Zhong, S. H. Ji, L. L. Wang, K. He, X. C. Ma, G. Gu, H. Yao, Q. K. Xue, X. Chen, and S. Y. Zhou, *Nat. Phys.* 9, 621 (2013).
15. http://xdb.lbl.gov/Section1/Table_1-1c.htm.
16. M. Bianchi et al., *ACS Nano* 6, 7009 (2012).
17. M. Scholz, J. Sánchez-Barriga, D. Marchenko, A. Varykhalov, A. Volykhov, L. V. Yashina, and O. Rader, *Phys. Rev. Lett.* 108, 256810 (2012).
18. H.-J. Noh, J. Jeong, E.-J. Cho, J. Park, J. S. Kim, I. Kim, B. G. Park, and H.-D. Kim *Phys. Rev. B* 91, 121110(R) (2015).
19. A. M. Black-Schaffer, A. V. Balatsky, and J. A. Fransson, *Phys. Rev. B* 91, 201411 (2015).

7. Search for proximity induced superconductivity on $\text{Bi}_2\text{Se}_3/\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ heterostructure

7.1 Introduction

In this chapter, we presented photoemission studies on the interplay between two important materials in condensed matter physics, topological insulators (TIs) and superconductors (SC). Such heterostructures are important because they can open a promising avenue for experimental observation of long sought Majorana fermions [1-3]. Majorana fermions are the zero mode particles and they can be experimentally observed in the vortex cores of the superconducting topological insulators. The bulk superconductivity is highly unlikely in TIs because of the extremely weak electron phonon-coupling and inherent 2D character of topological surface states (TSS) [4-6]. So far, bulk superconductivity has been observed only in Cu intercalated Bi_2Se_3 and in Bi_2Te_3 under pressure, with very low ($T_c < 5$ K) transition temperatures in both systems [7–9]. An alternative approach is to use artificial heterostructures, either lateral or layered, involving various superconductors and topological insulators in which the superconductivity in topological states would be induced by a superconducting proximity effect near their interfaces [10-16].

A recent study of TI/SC proximity effect used epitaxial grown 6-7 quintuple layer (QL) Bi_2Se_3 on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (BSCCO) superconducting substrate [17]. By the means of angle resolved photoemission spectroscopy (ARPES), the proximity induced superconducting energy gap in the TSSs of Bi_2Se_3 was reported to be observed with fairly large superconducting energy gap of ~ 15 meV, while bulk bands show only few meV superconducting gap. Superconducting energy gap is measured between the Fermi level of the TSSs of Bi_2Se_3 and the reference Fermi level taken from the Au plate as shown in Figure 7.1(b) (adopted from Reference 17). Additionally,

temperature dependence of such energy gap strongly indicates the proximity induce superconductivity (Figure 7.1(c)). If such large superconducting energy gap of 15 meV exists, these findings would be very promising for detecting the Majorana modes, as this would increase the level spacing's in the vortex cores by 3–4 orders of magnitude compared to p-wave superconductors, with a potential for even larger spacing if the E_F could be lowered by controlled filling of the topological surface state.

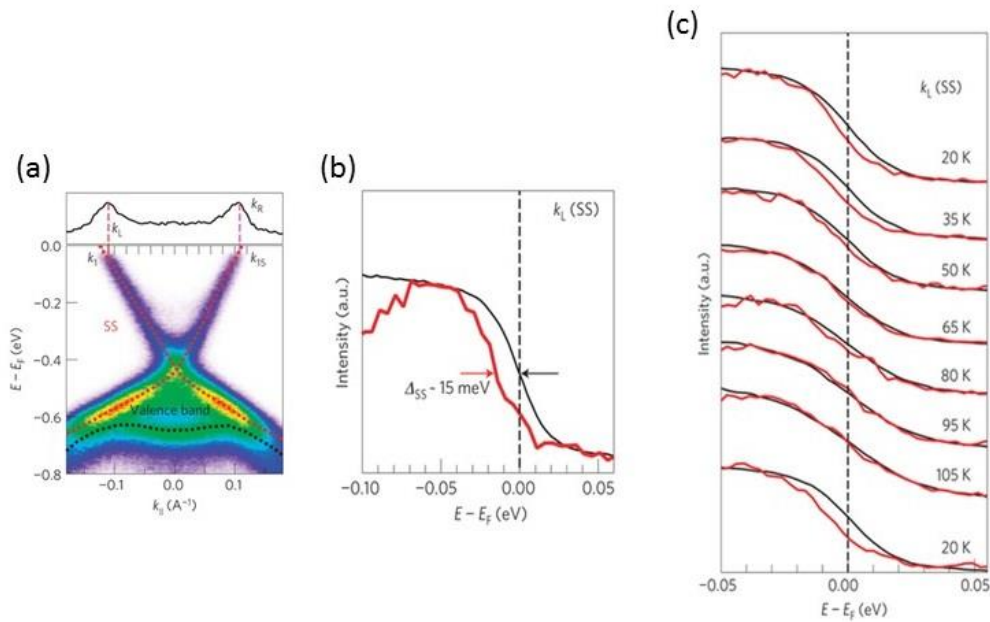


Figure 7.1. (a) ARPES measurement of Bi_2Se_3 grown on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (BSCCO) superconducting substrate. (b) Energy dispersive curve (EDC) taken from the left surface states along the dashed lines in (a), and black line represents the reference EDC taken from Au. (c) Temperature dependence of the superconducting energy gap. ARPES and EDCs are taken with 50 eV photon energy [17].

However, there are some inconsistent observations in that study that call for caution: (1) The ARPES study was done on ex-situ prepared films, requiring a delicate recovery procedure. (2) However, the superconducting energy gap was not observed in scanning tunneling microscopy (STM) on in-situ grown Bi_2Se_3 films. (3) The gap was detected only in the TSS and not in the

quantum well states (QWSs) (precursors of the bulk conduction band), even though the spatial extent of the QWS throughout the film thickness would favor even larger proximity effect in QWS. In addition, the proximity effect could only be propagated to the top by these QWS, as the topological surface state is otherwise completely decoupled from the interface. (4) The absence of the coherent quasiparticle peak in the topological surface state with such a large gap would suggest that the shift might be caused by some artifacts and not by a superconducting gap [18].

Nonetheless, the experimental results presented in Reference 17 are challenging to be repeated. Therefore, in this chapter of the thesis, we presented our detailed photoemission experiment on in-situ grown Bi_2Se_3 films on optimally doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (BSCCO) substrates in the thickness range from 0.5 QL to 15 QL.

7.2 Experiment

In our work we use molecular beam epitaxial method to grow atomically flat and clean Bi_2Se_3 films on superconducting $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (BSCCO) substrate in ultra-high vacuum (UHV) system with a base pressure of 7.5×10^{-10} torr. Single-crystal BSCCO samples with optimum oxygen doping ($T_c = 91$ K) were grown by the travelling floating zone method. Substrates were cleaved in-situ in order to start with clean surface. Resistance heating method was used to evaporate high purity Bi (99.999%) and Se (99.999%). The temperatures of the Bi source and Se source were run at 850 K and 490 K °C, respectively. We carried out two-step growth method to get better quality of films. We initially grow only few QL layers of Bi_2Se_3 at substrate temperature of 420 K and then increase substrate temperature to 470 K to deposit additional thicknesses of Bi_2Se_3 layers. The film thickness was varied between 0.5 QL and 15 QL. After growth we kept samples at 470 K for 10 min to produce smooth film surfaces. The ARPES experiments were

carried out on a Scienta SES-R4000 electron spectrometer at the U5UA beamline at the National Synchrotron Light Source, at the photon energy range from 17 to 52 eV and at sample temperature of 30 K. The total instrumental energy resolution was 10 meV at 17 eV and 12 meV at 52 eV photon energy. Angular resolution was better than 0.15° and 0.5° in the energy dispersing and nondispersing direction of the analyzer, respectively. Two spin detectors are mounted at the exit of the electron analyzer in order to perform 3-axis spin-resolved ARPES. The growth chamber is attached to the experimental chamber; thus all experimental procedure was carried without breaking the vacuum. The Fermi energy was calibrated by reference spectra taken from a clean gold metal which is placed on sample holder next to the film. Low-energy electron microscopy (LEEM) and microspot low-energy electron diffraction (μ -LEED) were performed on the ELMITEC LEEM III were performed at the U5 beamline at the NSLS in order to investigate crystalline structure of Bi_2Se_3 grown on BSCCO.

In the photoemission spectroscopy proper grounding the sample is crucial. In order to overcome any possible electrical charging problems, we have placed a thin indium foil under the BSCCO that melts at the growth temperature of Bi_2Se_3 and forms good electrical connection between the sample and the ground.

7.3 Results

We started our study with observing the electronic structure of BSCCO substrate after annealing a cleaved surface at 420 K for 15 minutes (Figure 7.2). In order to check whether or not such annealing effects the superconductivity, we perform ARPES measurements at 30 K with 30 eV photon energy. The Fermi surface of BSCCO substrate is shown in Figure 7.2(a) appearing as Fermi arcs, which is characteristic d-wave superconducting state. Also superimposed on the same image is the fermi surface of clean Bi_2Se_3 , observed as a small electron circle at the $\Gamma(000)$ point,

in order to show differences between fermi surface areas of the two specimens. In Figure 7.2(b) and (c), ARPES 2D intensities are shown for the nodal and anti-nodal region represented with dashed red line and solid black line in Figure 7.2(a), respectively. The superconducting gap energy measured by ARPES measurements for nodal and anti-nodal regions and superconducting gap size is measured to be ~ 25 meV (Figure 7.2 (d)). Additionally, a strong quasiparticle peak is also observed around 20 meV below the Fermi level for the nodal region (Figure 7.2 (d)). In conclusion, we eliminated the possibility that the electronic structure of BSCCO substrate is altered by annealing.

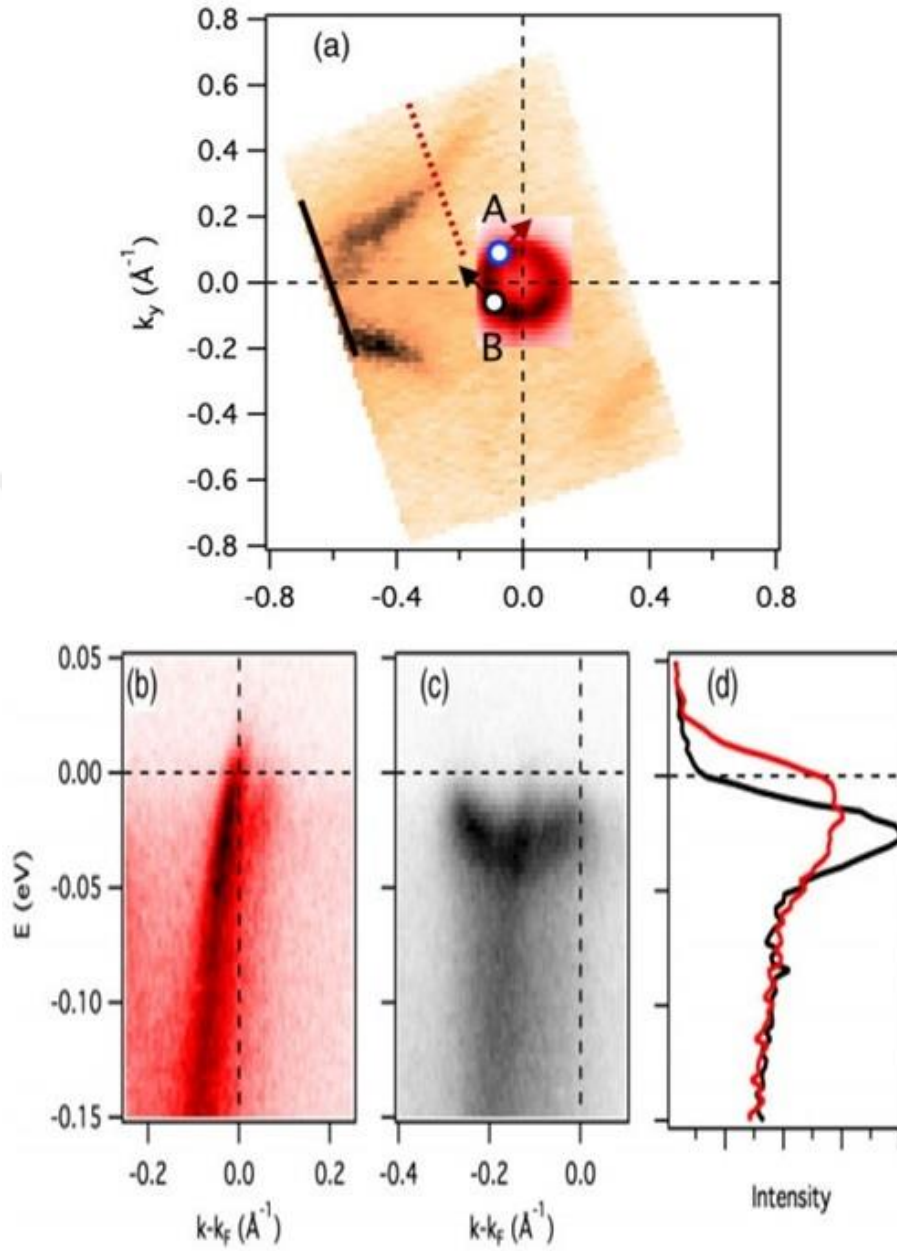


Figure 7.2.(a) Fermi surface of BSCCO substrate after annealing at 420 K red inset circle is the fermi surface of 10 QL Bi_2Se_3 . (b), (c) ARPES 2D intensity at the nodal and anti-nodal region, respectively. (d) EDCs at the nodal and the antinodal region indicated with dashed red line and solid black line in (a), respectively Measurements were recorded at 30 K with 30 eV photon energy.

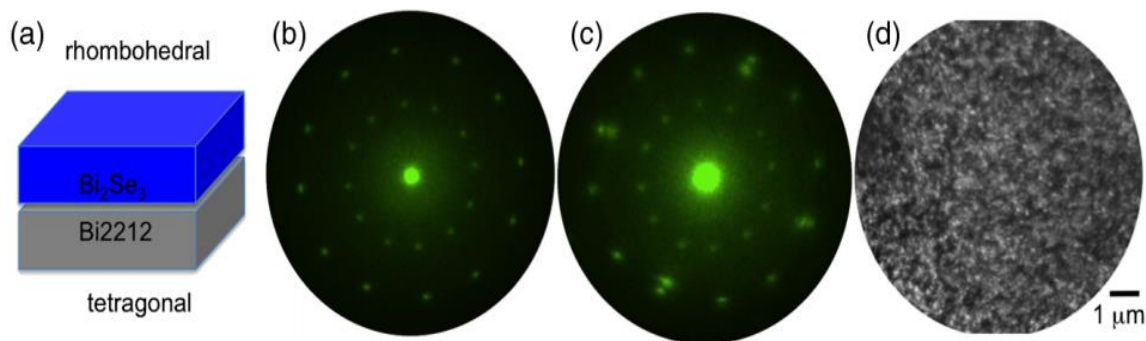


Figure 7.3. Structure of a Bi_2Se_3 film on a BSCCO substrate. **(a)** Schematic view of the studied structures. **(b)** μ -LEED image of a 10 QL Bi_2Se_3 film at 350 K. **(c)** μ -LEED image at $T=750$ K. **(d)** A real-space, dark-field LEEM image obtained from a diffraction spot corresponding to one of the domains. Bright features, representing the domains that contribute to the chosen diffraction spot. Images were taken at 20 and 18 eV in diffraction and real-space imaging modes, respectively.

The rhombohedral crystal structure of Bi_2Se_3 is composed of hexagonal (0001) atomic planes stacked in QL units with the in-plane lattice parameter $a = 4.14 \text{ \AA}$. The tetragonal crystal structure of BSCCO is made up of (100) planes having an in-plane lattice parameter $a = 3.82 \text{ \AA}$. Because of the mismatch of the in-plane lattice symmetry of the film and the substrate, there are two possible orientations of hexagonal (0001) planes (Bi_2Se_3) on top of (100) (BSCCO) by matching of atomic rows along the [100] or [010] direction of BSCCO with the $[\bar{2}110]$ direction of the Bi_2Se_3 (0001) planes. This results in two Bi_2Se_3 domains with crystalline orientation effectively rotated by 30° . We have performed μ -LEED measurements on 10 QL Bi_2Se_3 film grown on BSCCO. As seen in Figure 7.3(b) we indeed observe two hexagonal LEED patterns rotated by 30° with respect to each other, indicating the presence of two distinct crystallographic domains. Equal intensity of the two patterns indicates their equal population under the e-beam spot ($\sim 2 \text{ \mu m}$). We note that the diffraction pattern was independent of the position of the e-beam on the sample, indicating a high degree of the film's homogeneity. Figure 7.3(c) shows a μ -LEED pattern

after annealing at $T = 750$ K, which causes significant removal of the Bi_2Se_3 film and partial exposure of the BSCCO surface. We note this as the appearance of an additional, square diffraction pattern, which is attributed to the BSCCO (100) surface. The orientation of two Bi_2Se_3 domains on top of the BSCCO is evident from the alignment of the (10) LEED spots of hexagonal and square patterns, consistent with the idea of row matching of the two lattices. In Figure 7.3(d) we show the real-space dark-field LEEM image using the [100] diffraction beam of one of the Bi_2Se_3 domains. The white-gray contrast suggests that the domains are significantly smaller than $1\text{ }\mu\text{m}$. This also indicates that the ARPES data presented below will average over these two types of domains since the photon beam size ($<0.5\text{mm}$) in ARPES is comparable to the electron beam in LEEM measurement.

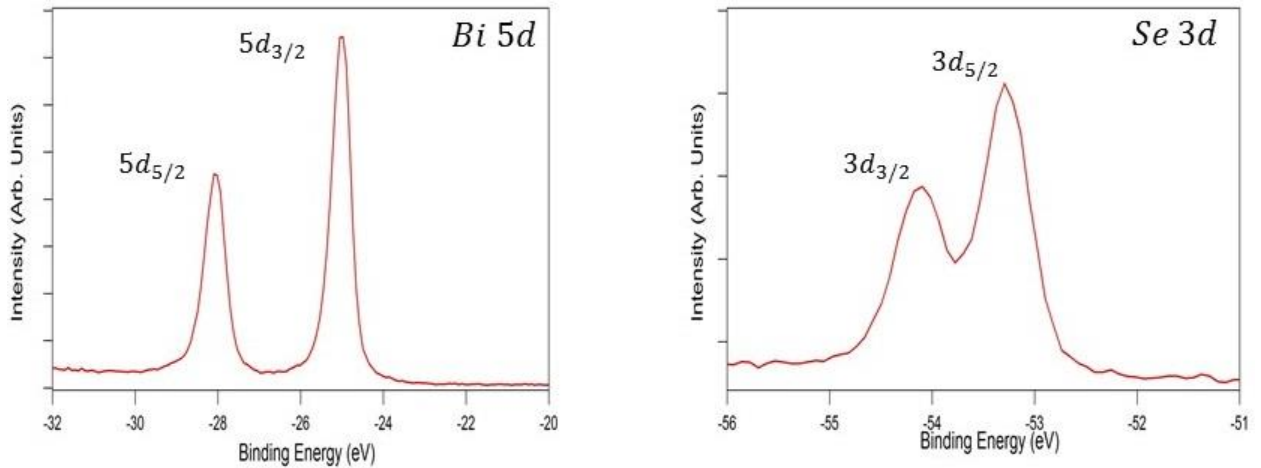


Figure 7.4. Core-level spectra of Bi 5d and Se 3d taken from 10 QL Bi_2Se_3 at 30 K with 104 eV photon energy.

Next, we checked the chemical environment of Bi_2Se_3 film by performing core-level photoemission spectroscopy. Bi 5d and Se 3d peaks are recorded with 104 eV photon energy and they are presented in Figure 7.4. We are able to resolve spin-orbit coupling in both Bi 5d and Se 3d.

The binding energies of Bi 5d_{5/2} and 5d_{3/2} are measured to be 25 eV and 28 eV, respectively. In addition, Se 3d_{5/2} and 3d_{3/2} core-level are located at 53.5 eV and 54.1 eV binding energies, respectively. We did not observe any peak formation near the Se 3d or Bi 5d indicating the absence of any other chemical phases except for Bi₂Se₃.

In order to show topological character of Bi₂Se₃ grown on BSCCO substrate we performed the spin resolved photoemission spectra. Spin polarization can be calculated by using photoelectron intensities in the left, I_L , and right side, I_R , of the Mott detector as $P = \frac{1}{S} \left(\frac{I_L - I_R}{I_L + I_R} \right)$. S is the Sherman function or efficiency of spin polarimeter, which is 0.17 in this particular work. Spin resolved photoemission measurement were done at the room temperature with 52 eV photon energy. In-plane components of the spin polarization are shown in Figure 7.5(a). Averaged spin polarization along the x and y direction is about 0.5 for at point A, while P_x component of the spin polarization switches from 0.5 to -0.5 from point A to B due to the change of the sign of the wave vector. This indicates the fully polarized surface states with helical spin texture as schematically illustrated in Figure 7.5(b).

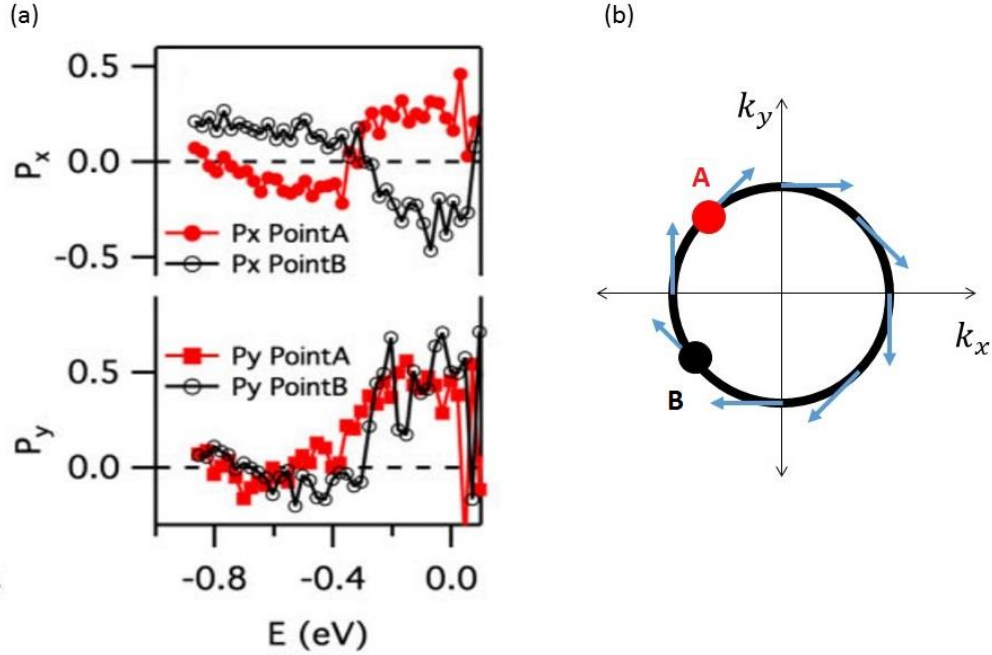


Figure 7.5.(a) The in-plane components of spin polarization of 10 QL Bi_2Se_3 grown on BSCCO substrate. Data recorded at 30 K with 52 eV photon energy. (b) Schematic representation of helical spin polarization on the surface of Bi_2Se_3 . Black circle and blue arrows represent Fermi surface and spin directions, respectively. A and B represent points where the spin polarized ARPES was performed.

So far we demonstrated that Bi_2Se_3 films grown on BSCCO substrate shows similar properties as Bi_2Se_3 films grown on other substrate, in terms of helical spin texture, core-levels and crystal structure (except for showing two different domains rotated 30° with respect to each other). In the proceeding section we will present number of ARPES measurements taken from Bi_2Se_3 films of different thickness all grown on BSCCO substrate, in order to investigate proximity induced superconductivity.

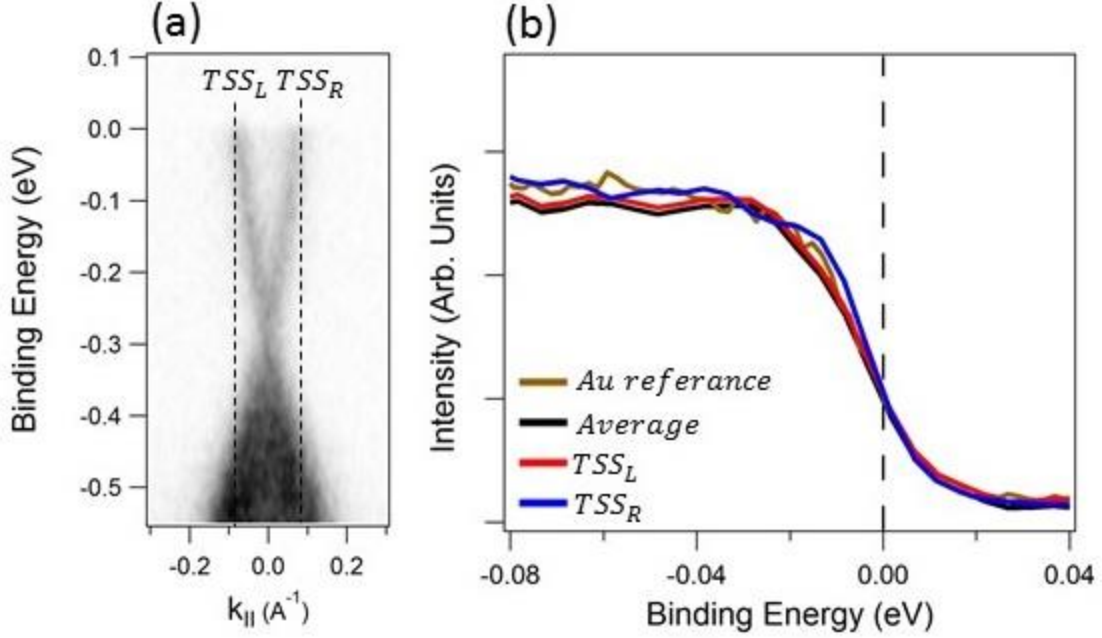


Figure 7.6.(a) ARPES 2D intensity of 15 QL Bi₂Se₃ grown on BSCCO substrate. Spectra is recorded at 30 K with 52 eV photon energy along the Γ -M direction. Left and right topological surface states are donated as TSS_L and TSS_R respectively. (b) leading fermi edges along the dashed line in (a) for TSS_L and TSS_R represented with red and blue solid lines respectively with Au fermi reference EDC (yellow solid line. Black solid line in (b) is averaged EDC over the momentum space.

We first performed ARPES experiment on 15 QL Bi₂Se₃ films grown on BSCCO substrate (Figure 7.6). ARPES 2D intensities were recorded with 52 eV photon energy and at 30 K sample temperature. The electronic structure shows clear Dirac like dispersion with Dirac point located at $k_{||}=0$ and 300 meV below the Fermi level. At this photon energy, the bulk bands are absent due to their low photoionization cross section at 52 eV photon energy. EDCs in the vicinity of the Fermi level is presented in Figure 7.6(b) for left topological surface state (TSS_L) and right topological surface state (TSS_R) as donated in Figure 7.6(a). Thick gold colored line represents the Fermi reference edge recorded from the Au plate. All the EDCs show the same Fermi level indicating absence of proximity induced superconducting energy gap. In order to take non-isotropic superconducting gap into account, EDC was averaged over the fermi circle, and it is also

presented in Figure 7.6(b). This averaged EDC shows the same Fermi level as all other EDCs, indicating that proximity induced superconductivity is absent.

We further extended our work to the bulk bands in order to look for possible superconducting gap in these bands. It is well known that TI materials are metallic only at the surface while the bulk is insulating. Therefore, the TSSs on the top and the bottom surface are completely decoupled from each other for thick films, which in the case of Bi_2Se_3 films was shown to be 6QL [19]. Furthermore, the bulk bands are the only bands that can give rise to the proximity induced superconductivity on the top surface, which is the one probed by ARPES. For this reason, we recorded ARPES 2D intensity with photon energy of 63.5 eV in order to show the bulk bands (Figure 7.7). At this photon energy, we are able to resolve the quantum well state (QWS), which is quantized version of bulk conduction band due to electron confinement perpendicular to sample surface. Bottom of the QWS is located at the 160 meV binding energy. The EDCs were obtained at different momentum points for left and right sides of Dirac cone and QWS as shown in Figure 7.7(a) with dashed lines. Resulting EDCs near the Fermi level are given with Au reference. Similar to TSS, neither of the QWS show any sign of the superconducting gap. Additionally, superconducting quasiparticle peak for both photon energies are also absent for bulk states. Therefore, we conclude that 15 QL Bi_2Se_3 grown on BSCCO does not show any superconducting character at the measurement temperature of 30 K.

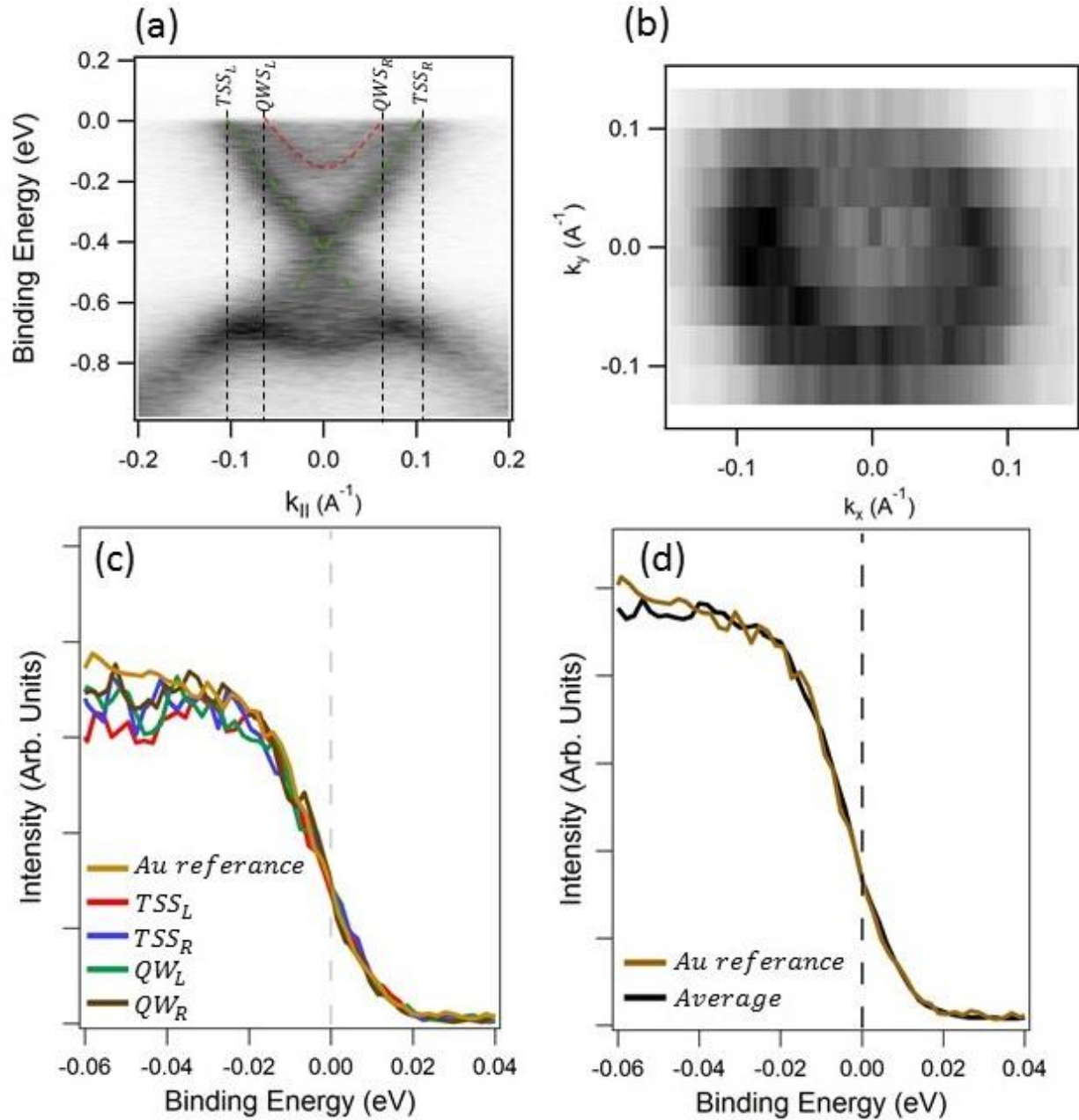


Figure 7.7. (a) ARPES 2D intensity of 15 QL Bi_2Se_3 taken at 30 K with 63.5 eV photon energy along the Γ -M direction. QWS and the TSSs are represented with dashed red and green line respectively. Fermi level crossing points of the QWS and surface states are represented with black and SS_L , QW_L , SS_R , QW_R are donated for the left and right TSSs and quantum well states respectively. (b) Fermi surface mapping of 15 QL Bi_2Se_3 that shows the characteristic circular fermi surface of Bi_2Se_3 . (c) EDCs curves along the dashed lines in (a) with Au reference Fermi edge. (d) Integrated EDC along the momentum region.

As we mentioned earlier, proximity induced superconductivity is depth dependent which can be probed by varying the thickness of the non-superconductor material. Because of negative result with 15 QL of Bi_2Se_3 grown on BSCCO, we studied thinner films. In the following few section ARPES experiments on 10 QL, 6 QL and 3 QL Bi_2Se_3 are presented in order to investigate possible superconducting gap formation in thinner films. As expected, for thinner films Dirac point shifts towards higher binding energy and it reaches 500 meV at 6 QL (Figure 7.8(b)). Below the 6 QL, as for 3 QL, the energy gap observed at Dirac point (Figure 7.8(c)) due to hybridization of the top and bottom surface. We investigated the proximity induced superconducting gap due to proximity effect by checking the EDC at left and right side of the Dirac cone as shown in Figure 7.8(a), (b), (c). Even for Bi_2Se_3 films as thin as 3 QL, the Fermi level is located at the same energy (Figure 7.8(d), (e), (f)) as in the Au reference.

In order to further support our result, we presented momentum integrated EDC in Figure 7.9 for all three samples. The integrated EDCs do not show the superconducting energy gap or quasiparticle peak formation indicating the absence of proximity induced superconductivity.

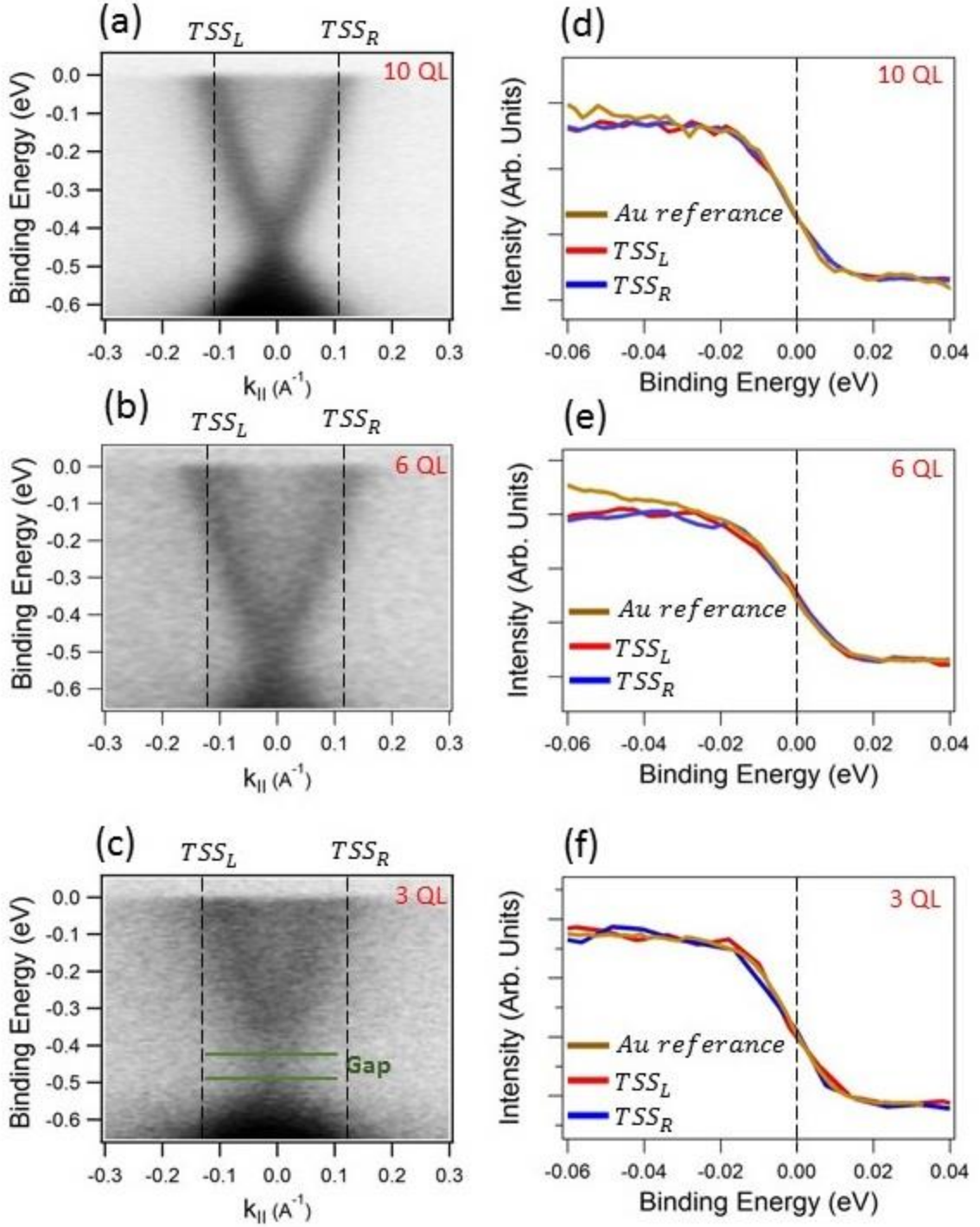


Figure 7.8. Thickness dependence electronic structure of Bi_2Se_3 . (a), (b), (c) ARPES 2D intensities of 10 QL, 6 QL, 3 QL Bi_2Se_3 taken at 30 K with 52 eV photon energy along the Γ -M direction. (d), (e), (f) corresponding EDCs left and right side of the Dirac cone as pointed on the top of each ARPES on the left side of panel.

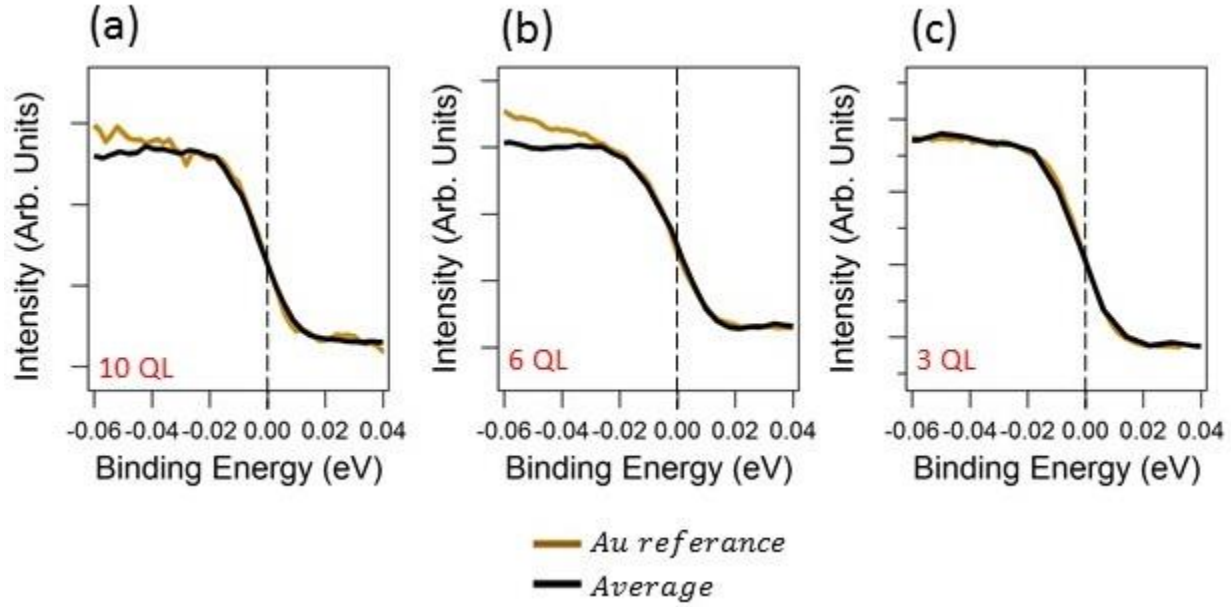


Figure 7.9. (a), (b), (c) Integrated EDCs of ARPES 2D intensities for 10 QL, 6 QL and 3 QL Bi_2Se_3 .

Furthermore, we decreased film thickness to 1 QL Bi_2Se_3 to search for proximity induced superconductivity. The ARPES data on such thin film shows good film quality by showing sharp TSS (Figure 7.10). For this thickness, the surface states at the bottom and top of the film strongly interact resulting in almost 300 meV energy gap at the Dirac point (Figure 7.10(a)). On the other hand, the thickness of 1 QL of Bi_2Se_3 is 9.56 Å, which is still large when compared to the coherence length of BSCCO, being ~ 1 Å [20]. The EDCs were obtained at the electron momentum ($k_{||}$) indicated in Figure 7.10(a) by dashed line. They are presented in Figure 7.10(b) with the Fermi level taken from the gold reference. Even for 1 QL, we did not observe any superconducting gap or quasiparticle peak showing the absence of proximity induced superconductivity on the film as thin as 1 QL.

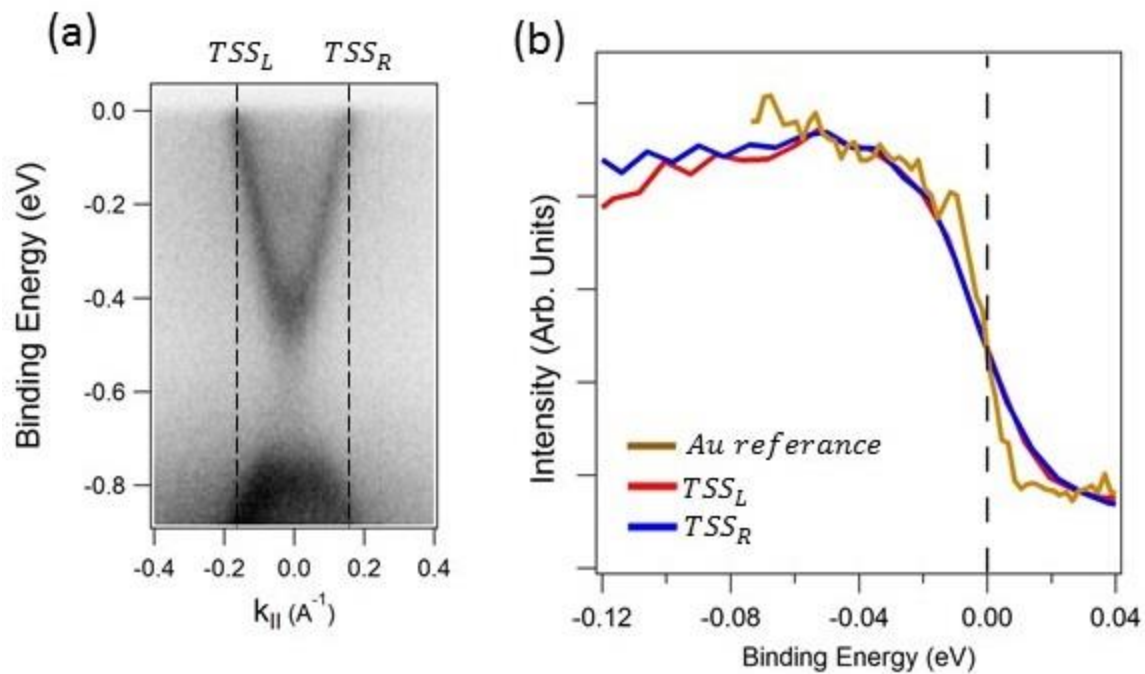


Figure 7.10. (a) ARPES 2D intensities of 1 QL Bi_2Se_3 on BSCCO substrate recorded at 30 K with 20 eV photon energy along the Γ -M direction. (b) Corresponding energy dispersive curves at momentum region indicated with dashed lines in (a).

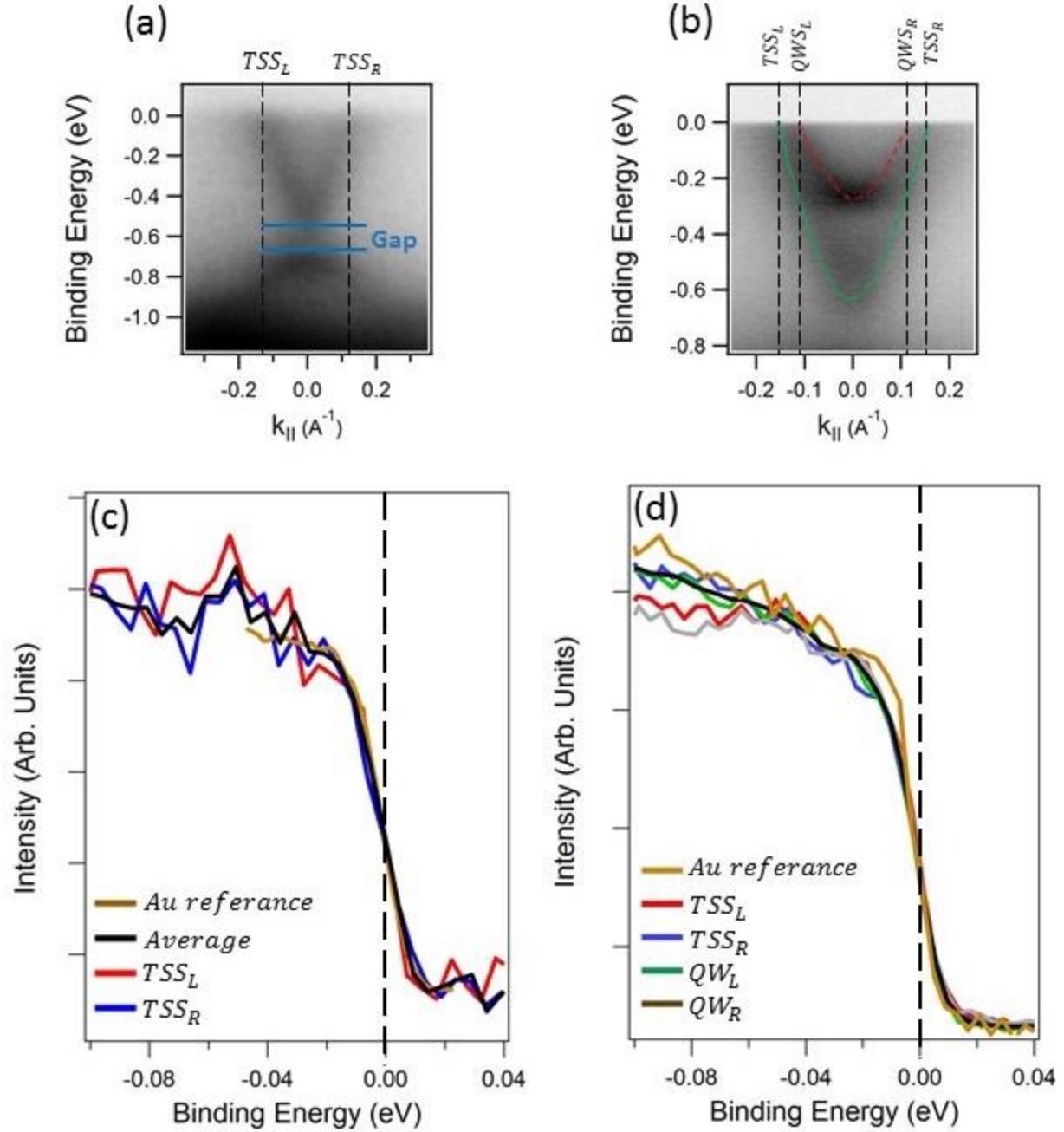


Figure 7.11. (a), (b) ARPES 2D intensity of 1 QL $\text{Bi}_2\text{Se}_3/\text{Bi}_2/\text{BSCCO}$ heterostructure taken at 30 K with 52 eV and 17 eV photon energies along the Γ -M direction, respectively. Dashed red and solid green line represent the bulk and surface states respectively. (c), (d), EDCs along the left and right surface and quantum well states with integrated energy EDCs along the momentum region.

In the next step, we first deposited bilayer of Bi on the surface of BSCCO substrate at the room temperature, then we growth 1 QL Bi_2Se_3 on top at 470 K forming the 1 QL $\text{Bi}_2\text{Se}_3/\text{Bi}_2/\text{BSCCO}$ heterostructure. The purpose of this is to change interface chemistry. Bi_2 is known to be a monolayer topological insulator whose Dirac point is located above the Fermi level. Resulting ARPES measurements are presented in Figures 7.11(a) and (b) for 52 eV and 17 eV photon energies, respectively. For low photon energy we also observe the bulk bands. Again, the gap at Dirac point is observed in the ARPES measurement for this 1 QL Bi_2Se_3 film (Figure 7.11(a)). Number of EDCs at different point of Fermi surface were obtained. However, none of the EDCs shows energy difference when compared to the leading edge of Au reference indicating again the absence of superconductivity. Furthermore, EDCs obtained from surface states or bulk states do not show quasiparticle peak.

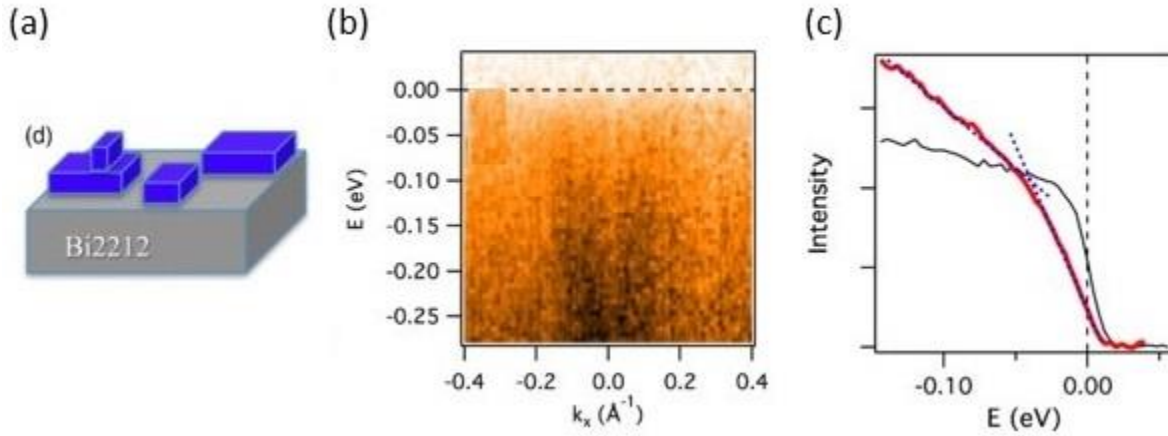


Figure 7.12.(a) A schematic representation of a sub-QL Bi_2Se_3 film. (b) ARPES 2D intensity of a ~ 0.5 QL Bi_2Se_3 film on a BSCCO substrate at 30 K with 52 eV photon energy along the Γ -M direction. The precursor of TSS is visible near the Γ point. (c) A characteristic EDC corresponding to the spectrum shown in (b) (red line) and a spectrum from an Au reference (black line). The EDCs from the film do not show any k dependence.

After having negative results on various thickness of Bi_2Se_3 on BSCCO substrate, we focused on 0.5 sub-QL of Bi_2Se_3 where we can only see the energy gap at the Fermi level (Figure 7.12(c)). As indicated in the schematic view (Figure 7.12(a)), this film necessarily forms an inhomogeneous structure, made of 1–2 QL thick Bi_2Se_3 segments and exposed BSCCO areas. The substantial background and broad features in the ARPES 2D intensity shown in panel (b) indicate a high degree of disorder and scattering. The undeveloped Bi_2Se_3 state suggests that the Bi_2Se_3 segments might be too small for the coherent k-space picture. At this thickness, the BSCCO substrate is still probed, but its states have also become very broad. The EDCs now show a clear shift of the leading edge by ~ 16 meV from the Fermi level. However, instead of a clear gap and a coherence peak, the spectrum shows a k-independent linear reduction in density of states at energies $|E| < 40$ meV, indicating that cooper pairs form spin-charge ordered states instead of becoming superconductor [21].

7.4 Conclusion

In conclusion, we find no evidence of proximity induced gaps at the Fermi surface of the top topological surface states within our experimental uncertainty of ~ 1 meV. This suggests that the proximity effect in heterostructures involving the interfaces between a d-wave superconductor and TI layers is strongly suppressed. We identify possible origins of a vanishing proximity effect to be: 1) a very short coherence length along the c axis in BSCCO superconductor, 2) a small Fermi surface of the TSS, 3) incompatible crystal and 4) pairing symmetries in the two materials, and 5) unfavorable effects of the strong spin-orbit coupling in Bi_2Se_3 on the d-wave pairing near the interface. Despite the negative results, this study not only gives important insights into the nature of low-energy electronic excitations in topological states, but it also offers a better understanding of cuprate superconductors and processes involving the interfaces of these materials. It also

suggests new experiments that could further test some of the proposed origins of a vanishing proximity effect in similar heterostructures. For example, it might be possible to increase the filling of the topological state by in situ doping to the point where the d-wave factor on its Fermi surface acquires a significant value [22]. Also, different materials, not necessarily TI, should be studied to test the role of the crystal structure of the interface and the strength of SOC in deposited material on the proximity effects near the BSCCO interface.

7.5 References

1. L. Fu and C. L. Kane, Phys. Rev. Lett. 100, 096407 (2008).
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. Z.-H. Pan, A. Fedorov, D. Gardner, Y. Lee, S. Chu, and T. Valla, Phys. Rev. Lett. 108, 187001 (2012).
5. H. Hochst and S. Gorovikov, J. Electron Spectrosc. Relat. Phenom. 144–147, 351 (2005).
6. Z.-H. Pan, E. Vescovo, A. V. Fedorov, G. D. Gu, and T. Valla, Phys. Rev. B 88, 041101 (2013).
7. Y. S. Hor, A. J. Williams, J. G. Checkelsky, P. Roushan, J. Seo, Q. Xu, H. W. Zandbergen, A. Yazdani, N. P. Ong, and R. J. Cava, Phys. Rev. Lett. 104, 057001 (2010).
8. M. Kriener, K. Segawa, Z. Ren, S. Sasaki, and Y. Ando, Phys. Rev. Lett. 106, 127004 (2011).
9. J. L. Zhang, S. J. Zhang, H. M. Weng, W. Zhang, L. X. Yang, Q. Q. Liu, S. M. Feng, X. C. Wang, and R. C. Yu, Proc. Natl. Acad. Sci. U.S.A. 108, 24 (2011).
10. D. Zhang, J. Wang, A. M. DaSilva, J. S. Lee, H. R. Gutierrez, M. H. W. Chan, J. Jain, and N. Samarth, Phys. Rev. B 84, 165120 (2011).
11. P. Zareapour, A. Hayat, S. Y. F. Zhao, M. Kreshchuk, A. Jain, D. C. Kwok, N. Lee, S.-W. Cheong, Z. Xu, A. Yang et al., Nat. Commun. 3, 1056 (2012).
12. S. Cho, B. Dellabetta, A. Yang, J. Schneeloch, Z. Xu, T. Valla, G. Gu, M. J. Gilbert, and N. Mason, Nat. Commun. 4, 1689 (2013).
13. F. Qu, F. Yang, J. Shen, Y. Ding, J. Chen, Z. Ji, G. Liu, J. Fan, X. Jing, C. Yang et al., Sci. Rep. 2, 339 (2012).
14. M. Veldhorst, M. Snelder, M. Hoek, T. Gang, V. K. Guduru, X. L. Wang, U. Zeitler, W. G. van der Wiel, A. A. Golubov, H. Hilgenkamp et al., Nat. Mater. 11, 417 (2012).
15. J. R. Williams, A. J. Bestwick, P. Gallagher, S. S. Hong, Y. Cui, A. S. Bleich, J. G. Analytis, I. R. Fisher, and D. Goldhaber-Gordon, Phys. Rev. Lett. 109, 056803 (2012).
16. F. Yang, F. Qu, J. Shen, Y. Ding, J. Chen, Z. Ji, G. Liu, J. Fan, C. Yang, L. Fu et al., Phys. Rev. B 86, 134504 (2012).
17. E. Wang, H. Ding, A. V. Fedorov, W. Yao, Z. Li, Y.-F. Lv, K. Zhao, L.-G. Zhang, Z. Xu, J. Schneeloch et al., Nat. Phys. 9, 621 (2013).
18. A proper grounding of samples is crucial for the stability of the measured energy of photoelectrons on the scale <1 meV. Typical clamping of BSCCO samples with Ta was proven to be insufficient as it often caused a poor ground connection and a finite, up to 10 meV,

energy shift, manifested as a gap in the ARPES spectra. To avoid this, we placed a thin indium foil under each BSCCO sample that melted during the film growth and formed a perfect ground connection during the ARPES experiments. Indium was also found to greatly improve the thermal contact.

19. Y. Zhang, K. He, C.-Z. Chang, C.-L. Song, L.-L. Wang, X. Chen, J.-F. Jia, Z. Fang, X. Dai, W.-Y. Shan, S.-Q. Shen, Q. Niu, X.-L. Qi, S.-C. Zhang, X.-C. Ma, and Q.-K. Xue, *Nature Phys.* 6, 584 (2010).
20. N. Kim, Y.-J. Doh, H.-S. Chang, and H.-J. Lee, *Phys. Rev. B* 59, 14639 (1999).
21. T. Valla, A. V. Fedorov, J. Lee, J. C. Davis, and G. D. Gu, *Science* 314, 1914 (2006).
22. T. Valla, Z.-H. Pan, D. Gardner, Y. Lee, and S. Chu, *Phys. Rev. Lett.* 108, 117601 (2012).

