NCKU
Aim for the Top University Project
2013 Annual Report

Research Project Title (Chinese)：拓樸絕緣體磊晶成長電子電荷和自旋傳輸研究與應用

Research Project Title (English)：Epitaxial growth and electronic, charge and spin transport studies on topological insulator films and their applications on spintronic devices

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I. Abstract

(1 page maximum, including 4~5 keywords)

Keywords: Topological insulators, molecular beam epitaxy, ARPES/SPEM, spintronic devices

Topological insulators (TIs) are a new class of insulators with topologically nontrivial band structures originated from strong spin-orbit coupling. Three dimensional (3D) TIs have been theoretically predicted and experimentally verified in a series of compounds, such as Bi$_{1-x}$Sb$_x$, Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$. These materials possess an insulating energy gap in the bulk and gapless surface state (SS) protected by time-reversal symmetry. The topologically protected SSs have been proposed to host a variety of interesting transport and magnetoelectric phenomena and are ideal platforms for spintronic devices.

The epitaxial growth and fundamental characterization TI films and will be carried in the coming three research years. The following are the key work to achieve step by step. TIs (Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$) epitaxial films will be synthesized by molecular beam epitaxy (MBE) on various substrates (Al$_2$O$_3$, Si etc).

1. In situ structural (RHEED), electronic (STM/STS) and ARPES/SPEM characterizations of the TIs.
2. Magnetic (Fe, Cr, Mn) and metallic (Ti) doping of the TIs by MBE.
3. Effort to synthesis TI nanostructures. (Wang, Huang)
4. TIs based multilayers and superlattices grown by MBE.
5. Transport and spin transport property study of TIs films and samples topped with magnetic layers (Mn, Cr, Co and Fe).
6. Fabrication of Hall structures using e-beam to study size effects.
7. Optical (dark and light conditions), transport, magnetic and magnetotransport characterization of the TIs and doped films and nanostructures.
8. Characterization of transistor: I-V, C-V and spin current-V$_g$: Study the surface channel and bulk contributions.
9. Fabrication of transistor on doped Bi$_2$Se$_3$ and Sb doped Bi$_2$Te$_3$.
10. Develop spintronic devices based on TIs multilayers and superlattices grown by MBE as mentioned.
11. Spin-torque prototype memory device based on the TIs and magnetic layers.
12. Thermoelectric transport and Spin Seeback effect studies.
13. Theoretical transport and simulation.

Our proposed organized team has the world class talents in the faculty as well as the state of the art facilities both for material preparation and characterizations, as well as device fabrication and analysis. PI J.C.A. Huang is experienced in grouping project such National Nano project. Huang is skillful in MBE growth of TIs and in situ surface, structural and magnetic characterizations by STM/STS/AFM/MFM. Co-PI S.J. Chang is experienced in MBE growth and device fabrication. Co-PI C. L. Wu is an expert using SPEM and ARPES (in synchrotron radiation center) for the crucial electronic characterizations.

Co-PI Wang is one of the world leading researchers in study TIs (he has published two Nature series articles related to TIs and papers in ACS Nano, advanced Materials and PRL). We expect to have breakthrough and fruitful results with the participation and help from Prof. Wang.
II. Content of Research Proposal

1. Background and Significance of Research

Topological insulators (TIs) are a new class of gapless material with topologically nontrivial band structures originated from strong spin-orbit coupling. The discovery of quantized spin Hall effect in two dimensional (2D) TI has stimulated intensive search for new TI systems associated with novel phenomena. Three dimensional (3D) TIs have been theoretically predicted and experimentally verified in a series of compounds, such as Bi$_{1-x}$Sb$_x$, Bi$_2$Se$_3$, and Bi$_2$Te$_3$. These materials possess an insulating energy gap in the bulk and gapless surface state (SS) protected by time-reversal symmetry. This metallic surface state is a two-dimensional electron gas with many unique features such as spin-momentum locking and robustness to localization by disorder. There exists the cone-shape dispersion with helical spin structure, i.e. Dirac cone, as showed in Fig. 1. Further, the interplay between magnetism and TI surface states is predicted to yield novel phenomena of fundamental interest such as topological magneto-electric effect, and quantized anomalous Hall effect, etc[4]. Therefore, TIs are ideal platforms for spintronic and quantum computational devices. These predictions have already triggered an active research for materials that provide experimental realization of such phenomena.

![Energy vs momentum of the states on the surface of 3D TI forms a Dirac cone.](image)

Ferromagnetism has been demonstrated in several magnetically doped TI crystals, including bulk crystal of Mn-doped Bi$_2$Te$_3$, as well as thin films of V-doped Sb$_2$Te$_3$, Cr-doped Sb$_2$Te$_3$, and Cr-doped Bi$_2$Se$_3$. In addition, ternary chalcogenide compounds ((Bi$_x$Sb$_{1-x}$)$_2$Te$_3$), which has similar tetradymite structure to the parent compound Bi$_2$Te$_3$ and Sb$_2$Te$_3$, is predicted and experimentally confirmed as a tunable TI system to engineering the bulk properties via the Bi/Sb composition ratio with stable topological surface state for the entire composition [9].
Some recent advances in the nanostructure of TIs such as nanoribbons of Bi$_2$Se$_3$ have been synthesized, allowing observation of the Aharonov–Bohm effect in the metallic surface state when a magnetic field is applied along the long direction of the nanoribbon [10], and molecular beam epitaxy has been used to grow thin films of Bi$_2$Se$_3$ with controlled thickness down to a single unit cell [11]. Such nanostructures and epitaxial multilayers are essential for many promising applications of TIs to spintronics and other fields. For example, the spin structure in Fig. 1b means that a charge current along the surface of the TI automatically yields a non-zero spin density; a heterostructure that combines a TI with a ferromagnet could allow the ferromagnet to be switched by passing a current through the topological insulator’s surface, and this would be a new type of spin torque device for magnetic memory applications [12]. The next important steps are to carry out direct transport and optical experiments on the metallic surface state to measure its conductivity and spin properties, and for these experiments improved materials with reduced residual bulk conductivity would be crucial. Because the main challenge to observing topological properties in real materials stems from the fact that as-grown Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ have a significant contribution from bulk conductivity. Therefore, their transport characterization (i.e. surface states in TIs) is hindered due to the contributions from both surface and bulk and obviously become a roadblock toward real device applications.

3D TIs, such as Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ share the same layered rhombohedral crystal structure in space group $D^{5}_{3d}$ (R3m). Each charge neutralized layer is formed by five covalently bonded atomic sheets, for example, Se-Bi-Se-Bi-Se in Bi$_2$Se$_3$, defined as a quintuple layer (QL) with thickness of ~ 1nm (Figure 2). The QLs are weakly bonded together by van der Walls interaction to form the crystal. These anisotropic crystallography characteristics are significant for controllable growth of TI materials. Recent experiment on the Bi$_2$Se$_3$ has demonstrated that when the thickness is reduced a cross over behavior from 3D to 2D in an oscillatory way can be observed.

Exciting experimental results have been reported in the past few years, these results are showing continuous progress in understanding the TI’s basic properties. However, still much work is needed to be done, from the epitaxial growth to characterization to realization of the application of these new materials, electronic detecting and manipulating the signal of surface states are still demanding. We believe this project is significant for both science and technology and significant results can be achieved by this project.

Fig. 2 Crystal structure of Bi$_2$Se$_3$ (Bi$_2$Te$_3$), a quintuple layer is indicated by red square.
Toward Applications

Present day’s electron devices are fast approaching the physical limits of miniaturization predicted by Moore. Therefore, smaller transistors, capacitors and other memories with lower power consumption are demanded. Spintronics is visualized to tackle this problem by avoiding resistive heating in such small devices in the near future.

A series of three-dimensional (3-D) topological insulators (TIs) have recently been discovered [1,9,10], which has gained great attention due to possible applications in spintronics. A TI is a gapped insulator in the bulk with gapless surface states featuring a Dirac cone electronic band structure. These gapless surface states, protected by time-reversal symmetry, are very robust. So far, topological surface states have been observed in Bi$_{1-x}$Sb$_x$, Bi$_2$Se$_3$, and Bi$_2$Te$_3$ [2,3,12]. Being able to grow high-quality thin films of TIs is an important step towards any realistic applications of these materials. In particular, the growth of TI thin films on industrial standard substrates such as Si, Al$_2$O$_3$, SrTiO$_3$ etc would enable further developments in material engineering and integration, such as bipolar or gradient doping, and heterostructure and/or superlattice fabrication using advanced semiconductor technologies. In this context, topological insulators (TI) are an attractive option for dissipationless spintronic devices.

Motivated by theoretical proposed tunable spin-related transport properties that based on manipulating the helical Dirac fermions (surface states) in topological insulators [12-15] through magnetic barrier, we propose the experimental study of spin transport in multi-terminal lateral geometries and Hall bar geometries in 3D TI thin film to gain understanding of those helical Dirac Fermions in TIs and how to control them. These will eventually lead to useful knowledge for constructing novel spintronic devices based on TIs.

We also would like to demonstrate the tunability of spin (charge) transports and related effects by engineering devices with top or bottom gate voltage to helical Dirac Fermion 3D TIs. Since both quantum Hall effect and spin quantum Hall effect states can be achieved by varying the global and local charge density from a back and top gate respectively.

On the purpose of these applications, to verify the surface dominated conduction from TIs and the Fermi level position within their bulk band gap are crucial [16,17].

In the proposal, we will optimize the TI materials through molecular beam epitaxy (MBE) growth, in-situ reflection high energy electron diffraction (RHEED), ex-situ X-ray diffraction (XRD) and atomic force microscopy (AFM) structural characterization as well as temperature dependent transport measurements and Angle-resolved photoemission spectroscopy (ARPES) (We have done most of these characterizations and have some important results). Study the surface channel and bulk contributions will be performed. The local (atomic) electronic information will be studied by scanning tunneling microscopy /spectroscopy (STM/STS). PI Huang’s group have successfully grown Bi$_2$Se$_3$ and Bi$_2$Te$_3$ films on Al$_2$O$_3$(0001) single crystalline substrate by MBE growth. Structural characterization has been done by in-situ RHEED and ex-situ XRD respectively.

A. Multiterminal TI spin valve
We perform spin transport measurements similar to previous reported spin transport measurement in graphene based spin valve devices. This mainly consists of charge and spin transport measurement in multiterminal spin valve devices to confirm existence of spin transfer in TIs. For this, combination of ferromagnetic/normal non magnetic electrodes will be used to detect spins with/without spin sensitive contacts. To understand the charge and spin transport, we first prepare prototype devices with non magnetic contacts as shown in Fig. 3.

![Fig. 3 Schematic drawing of a TI spin-valve device with top and back gates.](image)

After this we will perform both types of transport measurements by introducing a spin sensitive ferromagnetic contact in combination with normal contacts. At later stages spin injection and detection by ferromagnetic contacts will be performed and will be made with the results obtained earlier. These results help in understanding the influence of magnetic electrodes on the helical Dirac Fermion as well as giving information on the spin transport parameters in a TI.

Hanle spin procession measurement is typically used to extract the spin diffusion coefficient, spin life time and spin relaxation lengths and will not be performed. This is because perpendicular magnetic fields applied to quantum spin Hall states in TIs which will remove time reversal symmetry and thus helical Dirac Fermions. Rather, since an in plane magnetic field does not destroy the quantum spin Hall states, we perform length dependent spin valve measurement for different distances between injector and detector to be able to extract the spin relaxation lengths from a drift-diffusion spin model that takes into account the strong SOC. Since helical Dirac Fermions are robust to any impurity scattering, we expect the spin relaxation time in such devices to be similar to the momentum scattering time. These types of study helps to understand what kind of spin relaxation mechanism are dominant.

**B. Investigate the inversed spin Hall effect through Spin pumping**

In the field of spintronics, the inverse spin Hall effect (ISHE) converts a spin current, a flow of electron spins in a solid, into an electromotive force using the spin-orbit interaction. A novel charge pumping phenomenon in vertical FM/TI multilayers have theoretically been predicted. In the absence of any dc bias voltage, charge pumping is very sensitive to the presence or
absence of the surface gap $\Delta_{\text{surf}}$ and, therefore, can be employed to detect the presence of massive Dirac fermions by measuring the dc pumping voltage. We propose experimental setup as depicted in Fig. 4 for probing the inverse spin Hall effect (ISHE) in vertical FM/TI multilayers.

![Schematic drawing of spin pumping experiments on the FM/TI/Pt multilayers.](image)

**C. Thermoelectric transport in TIs**

In solids, both charge and heat flows are simultaneously generated when an electrochemical potential or a temperature gradient is present, leading to additional effect. In the 2-D electronic systems, the thermoelectric response in the quantum limit both transverse (Nernst effect) and longitudinal components (Seebeck effect) of the thermoelectric tensor have shown interesting feature, for example in graphene [24] or high T$_c$ superconductor cuprate. The relationship between the measured electrical conductivity and the Seebeck coefficient reveals how the chemical potential depends on the gate voltage or carrier density, which is dedicated by the energy dispersion. Therefore the thermoelectric transport coefficients can offer unique information and are complementary to the electrical properties.

![Schematic magneto-thermoelectric measurement setup related device drawing.](image)

The Nernst effect is the transverse voltage generated by a longitudinal thermal gradient in
the presence of a magnetic field. In Fig. 5, we proposed experiment utilized the idea of the transverse thermoelectric measurements as a probe of electron organization in topological insulators. The device is schematic illustrated in Fig. 5, a micron sized metal wire act as a heater by passing through current and provide a temperature gradient $\Delta T$ to the two ends of a topological film (dark brown strip), which give rise to a thermoelectric voltage $\Delta V$. The thermopower $S_{xx} = -\Delta V/\Delta T$. When a magnetic field is applied perpendicular to the TI plane, a transverse thermoelectric voltage is generated, so called Nernst effect. It is defined as $S_{yx} = E_y/\nabla T$. We will study the thermoelectric and magnetothermoelectric voltage on TI films to investigate the dependence of thermopower by tuning the carrier density through gate voltage and to realize the role of surface states in TI materials.

References:
2. Goal

(Please describe short, mid and long term goal.)

In the short term, we will optimize the TI materials through MBE epitaxial growth, in situ RHEED, ex situ XRD and AFM structural characterization as well as temperature dependent transport measurements and ARPES photoelectronic spectroscopy (We have done most of these characterizations and have some important results). In the mid-term, magnetic doping on these TI materials, synthesis of multilayer structures for different TI materials together with their magnetic and thermoelectric properties will be investigated as well (We have fabricated multiterminal spin valve type of devices to investigate their spintransport properties). In the long term, prototype TI based transistor will be fabricated, the characterization of transistor: I-V, C-V and spin current-Vg: Study the surface channel and bulk contributions will be performed. Spintronic devices based on TIs multilayers and superlattices grown by MBE as mentioned will be developed. Thermoelectric transport and Spin Seeback effect studies will be studied on those devices.

Material synthesis and characterizations

We have utilized our ultrahigh vacuum molecular beam epitaxy (MBE) to synthesize 3D TI films such as Bi2Se3, Bi2Te3, Sb doped Bi2Se3, and the recent discovered (Bi1-xSbx)2Te3 films for advanced device application. Their structural characterization will be performed via RHEED, and XRD, Raman spectroscopy and basic transport properties will be characterized by standard temperature dependent four probe/gate tuned Hall bar measurements. The electronic structure will be probed by using ARPES and SPEM. The local (atomic) electronic information will be studied by scanning tunneling microscopy (STM) and spectroscopy (STS). Utilize the previous mentioned characterization we can optimize the growth condition to meet the requirements of proposed device applications.

Proposed devices and measurement techniques

Our devices can be fabricated using standard photolithography/ e-beam lithography and etching process followed by thermal/e-beam evaporating metal contacts and liftoff process.

3. Research Methods
(For each year of the project, specify the research methods, step and difficulties of the project and how to solve.)

Core facilities and capability

Principle investigator J.C.A. Huang and Co-PI Chang are experienced in MBE growth, surface and structural analysis since his PhD study in 1980s. Huang has setup an epi-Center (see Fig.6) and dedicated a MBE system for the study of topological insulators. The MBE system allows in-situ study of TIs films by STM/STS. (see Fig. 7) Huang has developed skillful techniques in STM/STS as well as atomic force microscopy (AFM) and magnetic force microscopy (MFM) studies on epitaxial films including cross-sectional investigation on multilayer films. (see Fig. 8) Compared to the macroscopic probe such as ARPES, STM/STS can offer the atomic resolution of morphology and local density of states (DOS). So STM/STS is a powerful tool for the study of impurities or doping in TIs.

Fig 6. (Left) The epi-Center in NCKU (designed and in charge by PI Huang). Fig. 7 (Right) The UHV STM/AFM/MFM in NCKU (JOEL 4500, in charge by PI Huang).
Co-PI Prof. Kang L. Wang has years of experience in semiconductor devices, spintronics, and condensed matter physics. His research spans from the fundamental material growth and physics to nanoelectronics and spintronics devices involving II-VI, III-V, IV, graphene, and topological insulators (TI) as well metallic spin devices.

In the past two years, Wang has contributed to the development of TIs by using MBE, a powerful tool to grow high-purity TI materials with the ability to precisely control thin film thickness and doping. He demonstrated the surface states from MBE-grown Bi$_2$Se$_3$ thin films via ARPES, STM and low-temperature transport measurements. He has also demonstrated an effective approach to manipulate the surface states by tuning the Fermi level in TI nanoribbons, enabling the first observation of gate-controlled Shubnikov-de Haas and Aharonov-Bohm oscillations. Wang has a dedicated MBE system that is capable of selenium-, tellurium-, and
antimony-based TI growth, superlattice fabrication and precise magnetic impurity doping (Fe, Cr, Mn, and others). The group has a low-temperature Oxford dilution refrigerator system, capable of millikelvin temperatures, which will be used to probe the electromagnetic properties (Figure 9). In addition, the group also has a physical property measurement system (PPMS), which can be used to expedite characterization of the electronic and transport properties of MBE-grown TI thin films. The group also has an MOKE system for studying the spin properties based on optical Kerr’s rotation; he also has a micro Raman and other optical characterization systems for the proposed tasks. The core-facilities in California NanoSystems Institute (CNSI) and Nanoelectronics Research Facility (NRF) are also available for device fabrication including 10 nm e-beam writer as well as other characterization tools for investigating the surface states and interconnect properties of nanoscale TIs. Wang’s group has recently successfully demonstrated the manipulation of surface states in nano-ribbons of Bi$_2$Te$_3$ made by chemical synthesis, through transport measurements. He also developed high quality topological insulator thin films grown by molecular beam epitaxy (MBE) on different substrates.

Co-PI Prof. C.L. Wu is skillful in using Synchrotron facility on study of electronic property. To comprehensively realizing TIs, He proposes to use both focused and unfocused soft x-ray for photoelectron spectroscopic studies to construct the electronic structures of TIs in a three-dimensionally perspective view. In this project, we plan to use a UHV analysis system (shown in Fig. 10, starting on May 2012) dedicated to photoelectron spectroscopic studies of polar heterojunction system, which also has integrating capabilities for SPEM end station in National Synchrotron Radiation Research Center (NSRRC, in HsinChu, Taiwan) and NSRRC’s beamlines. A three-dimensional view of electronic structure of TI surfaces and heterojunctions will be presented in two types of spectromicroscopic studies: conventional normal and novel cross-sectional studies on photoelectron spectroscopy (PES) and scanning photoelectron spectromicroscopy (SPEM). The results of these novel issues of spectroscopic and microscopic acquisition/analysis will be an important aspect of TIs activities. We also hope this project could be a platform for Taiwan’s scientists and researchers to study on TIs.
Co-PI Prof. Y. T. Lu is now the chairman of the Physics Department and Director of National Center of Theoretical Sciences (NCTS) of the south division. He has established associations and cooperation of many theorists; and he will seek to establish links and exchanges researchers worldwide to study the TIs.

**Plan of this proposal**

The general goal of this research is to realize quantum spin Hall transistor that made of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ TIs with multiple terminals. Spin valve devices with different distance between injector and detector electrodes will be prepared. Result of such measurement will be used for subsequent realization of spin transport in TIs. From the above theoretical predictions and experimental results, we can understand that the research of TIs has just begun. Although some exciting and excellent results have been reported, still many issues remain to be answered, as summarized below.

Besides the advanced device proposed above, the growth and fundamental characterization TI films and multilayers will be carried **step by step** (in the coming **three research years**):

**In the first year**

1. TIs (Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$) epitaxial films will be synthesized by molecular beam epitaxy (MBE) on various substrates (Al$_2$O$_3$, Si, SrTiO$_3$, etc). (Huang, Wang)
2. In situ structural (by RHEED), electronic (by UHV STM/STS) and ARPES/SPEM characterizations of the TIs. (Wu, Huang)
3. Magnetic (Fe, Cr, Mn) and metallic (Ti) doping of the TIs by MBE. (Huang, Wang)
4. Effort to synthesis TI nanostructures. (Wang, Huang)
5. TIs based multilayers and superlattices grown by MBE. (Huang, Wang)

**In the second year**

6. Transport and spin transport property study of TIs films and samples topped with magnetic layers (Mn, Cr, Co and Fe). (Huang, Wang)
7. Fabrication of Hall structures using e-beam to study size effects. (Wang, Chang)
8. Optical (dark and light conditions), transport, magnetic and magnetotransport characterization of the TIs and doped films and nanostructures. (Wu, Huang)
9. Characterization of transistor: I-V, C-V and spin current-V$_g$: Study the surface channel and bulk contributions (Wang)

**In the third year**

10. Fabrication of transistor on doped Bi$_2$Se$_3$ and Sb doped Bi$_2$Te$_3$. (Wang, Chang)
11. Develop spintronic devices based on TIs multilayers and superlattices grown by MBE as mentioned. (Wang, Chang, Huang)
12. Spin-torque prototype memory device based on the TIs and magnetic layers. (Wang, Chang, Huang)
III. Result and Discussions

(Please highlight the results which are World-leading or Taiwan-leading.)

In the past, we have successfully grown high quality Bi$_2$Te$_3$ and Bi$_2$Se$_3$ TI thin films by MBE. Some results have been carried out recently and will list below.

A. Controlling the electronic band structure by tuning the growth parameters

In the recent, we have devoted efforts in optimizing the growth condition and controlling the electronic band structure by tuning the growth temperature. Electronic band structures of our Bi$_2$Te$_3$ TI films have investigated by ARPES at NSRRC, as shown in Fig. 11, which demonstrated that there exist surface states and its electronic properties can be very sensitive to the growth conditions and strongly correlated to the stoichiometric of Bi$_2$Te$_3$.

Fig. 11. Electronic band structures of Bi$_2$Te$_3$ films measured by ARPES, the stoichiometric of Bi$_2$Te$_3$ measured by XPS, a strong correlation of the Dirac point position (blue circle) and Te/Bi atomic ratio (red square) can be addressed.

B. Electric- and magneto-transport measurements on the TI-Hall bar and TI-FET devices

To be able to tune the Fermi energy of the TI thin films is an important step to manipulate the surface states of the TIs, prototype Hall bar and FET type of devices have been fabricated and their transport properties have been investigated. As showed in Fig.12, and Fig. 13, we have measured a Hall bar device by photo- and ebeam-lithography and CF$_4$ RIE etching process, its temperature dependence and magnetic field dependence transport properties were measured by
PPMS with lowest temperature 2K and highest magnetic field up to 9 Tesla. Temperature dependent measurement resistance and the mobility can reach to about $1.1 \times 10^3$ cm$^2$/V-s, which is compatible to the value reported in the literature; its magnetic field dependent measurements is performed at 2K, we observed a weak antilocalization (WAL) phenomena, which is caused by the Berry phase and is the signature of 3D topological insulators.

![Image of TI Hall bar device](image1.png)

**Fig. 11.** TI Hall bar device: (a) Real device image (Bi$_2$Te$_3$ films), (b) illustration of measurement setup, (c) and (d) are the temperature dependent measurements, (e) and (f) are the magnetic field dependent measurements.

![Image of TI Hall bar device](image2.png)

**Fig. 12.** TI Hall bar device: (a) Real device image (Bi$_2$Te$_3$ films), (b) illustration of measurement setup, (c) and (d) are the temperature dependent measurements, (e) and (f) are the magnetic field dependent measurements.

C. **Optimal tuning of atomic and electronic structures in MBE-grown Bi$_2$Te$_3$-xSe$_x$ topological insulator alloys**

To explore and manipulate the unique property that arises from the surface states of TIs provides opportunities for studying the novel physics. For example, Dirac fermions and Majorana fermions, which are important for quantum computation in the future. However, 3D TIs samples such as Bi$_2$Se$_3$ and Bi$_2$Te$_3$ are conducting in the bulk, and their transport properties are always
dominated by the bulk current. To get a bulk insulating TI material is very crucial to explore the novel surface transport properties of topological insulators. A new TI material with a bulk insulating state is obviously important and must be sought. Such materials include tetradymite-structured Bi$_2$Te$_2$Se nanoplates and nanoribbons, which have a basic Te-Bi-Se-Bi-Te quintuple-layer (QL) unit. We have fabricated Bi$_2$Te$_{3-x}$Se$_x$ films with careful control of the mixing ratio of Bi$_2$Se$_3$ to Bi$_2$Te$_3$ by tuning the Bi:Te:Se flux ratio in MBE.

The Se (and Te) content of the Bi$_2$Te$_{3-x}$Se$_x$ films can be accurately estimated from the lattice spacing, which declines linearly with the Se content, $x$. The surface of the Bi$_2$Te$_{3-x}$Se$_x$ films reveals characteristic triangular terrace-like quintuple layers whose sizes decrease monotonically as $x$ increases. As depicted in Fig. 13, through the structural characterization of the MBE-grown Bi$_2$Te$_{3-x}$Se$_x$ films have shown how the structural evolution as the Te/Se ratio varies.

Fig. 13 Structural characterization of MBE-grown Bi$_2$Te$_{3-x}$Se$_x$ thin films: (a) RHEED patterns for electron beam incident at [2 1 1 0] and (b) at [0 1 1 0] of sapphire substrate; (c) X-ray diffraction from 20 QL pure Bi$_2$Te$_3$ film, the Bi$_2$Te$_{3-x}$Se$_x$ films, and pure Bi$_2$Se$_3$ film, (d) zoom-in on (0021) peaks of all films, (e) dependence of c-axis lattice constant from (0021) peak on Te/Se flux ratio, and (e) dependence of lattice constant on substitution ratio of Se atoms, obtained from Vegard’s law.

The Se (and Te) content of the Bi$_2$Te$_{3-x}$Se$_x$ films can be accurately estimated from the lattice spacing, which declines linearly with the Se content, $x$. The surface of the Bi$_2$Te$_{3-x}$Se$_x$ films reveals characteristic triangular terrace-like quintuple layers whose sizes decrease monotonically as $x$ increases (Fig. 14).
Fig. 14 Large-scale AFM images (size: 2\(\mu\)m \(\times\) 2\(\mu\)m) of pure Bi\(_2\)Te\(_3\), Bi\(_2\)Te\(_{3-x}\)Se\(_x\), and pure Bi\(_2\)Se\(_3\) films with thickness of 20nm.

The electronic structure of the thin films was confirmed by angle-resolved photoemission spectroscopy (ARPES). Figure 15(a) shows the ARPES result in Bi\(_2\)Se\(_3\) film, which is taken at 20eV of photon energy. The sharp surface states and 2DEG state demonstrates that the Bi\(_2\)Se\(_3\) sample is a well-ordered and high quality film. Figure 15(b)-(d) display the ARPES of the MBE-grown Bi\(_2\)Se\(_3\), Bi\(_2\)TeSe\(_2\), and Bi\(_2\)Te\(_2\)Se films measured at photon energy of 22eV, respectively, revealing single-Dirac-cone like surface states for the Bi\(_2\)Te\(_{3-x}\)Se\(_x\) films. The Dirac point of all films is identified from the crossing of the surface state. It is noticed that the electronic structure of Bi\(_2\)Te\(_{3-x}\)Se\(_x\) approaches that of the Bi\(_2\)Se\(_3\) film and the Dirac state becomes an isolated Dirac cone as the Se content increases. The Dirac points \(E_D\) of Bi\(_2\)Se\(_3\), Bi\(_2\)TeSe\(_2\), and Bi\(_2\)Te\(_2\)Se films are 340meV, 380meV, 430meV, respectively. The position of Dirac point lowers continuously and the distance between Dirac point and Fermi level increases monotonically with increasing Te content.

Fig. 15 (a) Band mapping results for MBE-grown Bi\(_2\)Se\(_3\) film along \(\Gamma-K\) direction obtained at a photon energy 20eV; (b)-(d) for Bi\(_2\)Se\(_3\), Bi\(_2\)TeSe\(_2\), and Bi\(_2\)Te\(_2\)Se films along \(\Gamma-K\) direction obtained at a photon energy at a photon 22eV, respectively.
The extent of this effect can be attributed to the stronger spin orbit coupling (SOC) in Bi$_2$Te$_2$Se than in Bi$_2$TeSe$_2$ and Bi$_2$Se$_3$. The amount of surface electron density can be estimated from the occupied area of Fermi surface (FS) on the whole Brillouin zone (BZ). The surface carrier concentration $n_s$ of Bi$_2$Se$_3$, Bi$_2$TeSe$_2$, and Bi$_2$Te$_2$Se can be estimated as $7.07\times10^{12}$ cm$^{-2}$, $1.19\times10^{13}$ cm$^{-2}$ and $1.34\times10^{13}$ cm$^{-2}$, respectively. The Bi$_2$Te$_2$Se exhibits the largest surface concentration in these films.

Transport-related measurements of the Bi$_2$Te$_{3-x}$Se$_x$ thin films are essential for determining its material properties. Standard four point measurements were made to determine the temperature-dependent resistivity ($\rho$ versus $T$) of the Bi$_2$Te$_{3-x}$Se$_x$ films. From the $\rho$-$T$ curves of the Bi$_2$Te$_{3-x}$Se$_x$ films with different Se contents, we can get the electric transport properties vary with the structure of Bi$_2$Te$_{3-x}$Se$_x$, the resistivities at 250 K and 30K. As presented in Fig. 16, the resistivities at 250 K and 30K are plotted as functions of Se content. The resistivity increases rapidly as the Se content increases, reaching its highest value around 17.5m$\Omega$-cm (15m$\Omega$-cm) when Te/Se = 2.03, decreasing again as the Se content increases. To compare the contributions from both the surface and bulk of these films, their bulk carrier concentrations $n_b$ were measured by the Hall measurements in a van der pauw configuration. The bulk concentrations $n_b$ of Bi$_2$Se$_3$, Bi$_2$TeSe$_2$, and Bi$_2$Te$_2$Se are $3.6\times10^{19}$ cm$^{-3}$, $1.8\times10^{19}$ cm$^{-3}$, and $1.5\times10^{19}$ cm$^{-3}$, respectively. The ratio of surface carrier concentration (estimated from ARPES data) to the total carrier concentration of individual film, $n_s/(n_s+n_b)$ ($t$ is the film thickness), is estimated to be 0.089, 0.248, and 0.309, respectively. In presented work, Bi$_2$Te$_2$Se film exhibits higher surface carrier concentration (higher surface state contribution) and resistivity, which is benefit for further low power spintronic devices due to contributing large spin polarized carriers and reducing of scattering from bulk carriers.

Fig. 17 Resistivity of ten Bi$_2$Te$_{3-x}$Se$_x$ samples with various Se contents at 250K (30K).

This work demonstrates that Bi$_2$Te$_2$Se has the best structural and electronic transport
properties of any of the members of the Bi$_2$Te$_{3-x}$Se$_x$ family. In addition, the MBE-grown Bi$_2$Te$_{3-x}$Se$_x$ film can provide a platform for investigating the magnetic interaction and electronic structure tailoring in topological insulators by co-substitution magnetic and non-magnetic elements.

The ARPES results provide evidence of single-Dirac-cone like surface states. Bi$_2$Te$_{3-x}$Se$_x$ with Se/Te-substitution leads to tunable surface states with a single Dirac cone. Resistivity increases rapidly with Se content and reaches a maximum when Te:Se=2:1. The results demonstrate that optimal tuning of Bi$_2$Te$_{3-x}$Se$_x$ films in the vicinity of Bi$_2$Te$_2$Se is useful for further investigation of novel topological properties and device applications.

In summary, from the results presented above, we have made a lot of progresses in both making TI materials as well as fabricating TI devices. In combination of both material and device efforts we have made so far, the next phase of this proposal will have very promising outcome.
IV. Contributions

(Please complete the table as below and describe the major contributions.)

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<td>1. G. Venkataiah(^a), J.C.A. Huang(^b), P. Venugopal Reddy(^a), “Magnetic, electric and thermoelectric behavior of electron-doped La(_{1−x})Sb(_x)MnO(_3) (x = 0.05, 0.10 and 0.15) manganites”, <em>Journal of Alloys and Compounds</em>, 562, 15 June 2013, 128–133 (SCI)</td>
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<td>2. M. K. Lee(^1), L. S. Xu(^2), V. V. Marchenko(^3), R. L. Wang(^1,2), R. J. Chen(^4), S. Guo(^4), C. P. Yang(^7), J. C. A. Huang(^1)*, “Effect of Ge and Al substitutions on exchange bias in Ni-Mn-Sb alloy”, <em>J. Appl. Phys.</em>, 113, 17D712 (May 2013) (SCI)</td>
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<td>3. Kai-Wei Tsai(^5), Tsung-Hsun Lee(^b,c), Jin-Han Wu(^a), Jing-Yuan Jhou(^5), Wei-Shun Huang(^b), Sung-Nien Hsieh(^a), Ten-Chin Wen(^a,d,<em>), Tzung-Fang Guo(^b,d,</em>), J.C.A. Huang(^c,d,*), “Antagonistic responses between magnetoconductance and magnetoelectroluminescence in polymer light-emitting diodes”, <em>Organic Electronics</em>, 14 (May 2013)</td>
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4. Shu Hsuan Su†, Hsin-Hsien Chen†, Tsung-Hsun Lee†, Yao-Jane Hsu†, and J. C. A. Huang†,†,§,*,

5. S.H. Chiu†, J.C.A. Huang**,†
“Characterization of p-type CuAlO2 thin films grown by chemical solution deposition”, Surface and Coatings Technology, 231, 239-242, SEP 2013 (SCI)

6. Wei-Shun Huang1, Zhe-Rui Xu1, Bin Hu2, Tzung-Fang Guo1,3,a), J. C. A. Huang3,4,a) and Ten-Chin Wen5,

Research 2 SSCI papers

Research 3 A&HCI papers 1
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vacancy enhanced room-temperature ferromagnetism in Co-doped ZnO”, Applied Physics Letters, 88, 242507 (2006). (Citation times: 257)
## V. Expenses

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