The Thesis Committee for Yuxuan Chen
Certifies that this is the approved version of the following thesis:

Molecular Beam Epitaxy of Topological Insulator Bi_2Se_3

APPROVED BY
SUPERVISING COMMITTEE:

Supervisor: ______________________________
Chih-Kang Shih

____
Alejandro L. de Lozanne

Molecular Beam Epitaxy of Topological Insulator Bi_2Se_3

by

Yuxuan Chen, BS

Thesis

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Dedication

This thesis is dedicated to my parents, Jianping Chen and Shi'e Jia, who always support me and encourage me to continue my pursuit of truth.

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I am indeed grateful to my supervisor, Dr. Shih, for providing me the opportunity to study this interesting topic and giving me advices and critics which accelerated my progress.

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Abstract

Molecular Beam Epitaxy of Topological Insulator Bi_2Se_3

Yuxuan Chen, MA
The University of Texas at Austin, 2012

Supervisor: Chih-Kang Shih

In this thesis, I show my effort in growing atomically flat Bi_2Se_3 thin films using molecular beam epitaxy (MBE) method. Bi_2Se_3 is a kind of topological insulator, whose exotic surface states have been found in the samples that I grew.

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Introduction

Topological insulators (TIs) constitute a new category of condensed matter which has recently been studied intensively[1]. It has drawn special attention because of its prospects for practical application in spintronics and quantum computing, and because of the possibility of finding a quasi-particle Majorana fermion at its interface with superconductors.

A TI possesses these properties: 1) it has a bulk energy band gap; 2) it has helical gapless surface states that result from strong spin-orbit coupling (SOC); 3) its surface states are robust, protected by time reversal symmetry; and 4) the surface states have an odd number of Dirac cones. TIs are distinguished from normal insulators by topological order: the topology of its band structure is different from that of a normal insulator. Mathematically, this difference is represented by a topological invariant Z2[2].

Compared to the other kinds of TIs, the binary compound Bi_2Se_3 has several advantages: 1) it is a three dimensional material and has two dimensional surface states; 2) it is a crystalline compound, so it can by prepared with high purity; 3) it has a large, (compared to the other TIs) bulk band gap of 0.3 eV; 4) the Dirac point of the surface states is in between the bulk band gap.

Usually, bulk Bi_2Se_3 is synthesized by mixing high purity bismuth (Bi) and selenium (Se) powder stoichiometrically and heating the mixture to form chemical bonds. However, due to the versatile nature of Se, such bulk crystals usually contain a large number of Se vacancies which push the Fermi level into the conduction band[3]. As a result, the bulk electrons will dominate transport in TI, submerging the desired exotic surface properties.

Molecular beam epitaxy (MBE) can overcome this problem by introducing extra Se during layer-by-layer growth. There are three critical parameters in the MBE process: substrate temperature, and Se and Bi source temperatures. By tuning these three parameters carefully, one can get atomically flat crystalline Bi_2Se_3 thin films. This thesis shows that I have grown such Bi_2Se_3 thin films successfully.

Apparatus

The topological insulator molecular beam epitaxy (TI-MBE) system contains these major parts: 1) ultra-high vacuum (UHV) chamber with load lock and sample transport devices; 2) effusion cells; 3) substrate heating stage; 4) quartz crystal monitor; 5) reflection high energy electron diffraction (RHEED) system.

The UHV chamber is made of stainless steel and has a load lock. It can reach 1.2×10^{-10} Torr after being baked to ~120°C. UHV is necessary for growing high purity material, as the number of undesired atoms and molecules falling onto the sample must be reduced as much as possible. The load lock is also needed for the purpose of loading samples from air into the UHV environment without jeopardizing UHV. We use a 30 inch transfer arm to deliver a sample into the UHV chamber, and use a wobble stick to take the sample from the transfer arm and mount it on the heating stage where substrate treatment and thin film deposition take place.

The effusion cell for Bi is a commercial Knudsen cell, while the cell for Se is home-built. Both are controlled by feedback electronics, so they can maintain the source materials at stable temperatures and evaporation flux.

The home-made substrate heating stage has three heating functions: Joule heating, radiation heating, and electron beam bombardment. For highly doped Si, the most commonly used substrate in our lab, Joule heating is used to outgas the substrate and melt its surface, in order to obtain the desired surface reconstruction. For insulating substrates, radiation and electron beam bombardment are used.

A quartz crystal monitor is used to calibrate the deposition rate of the source material. The model we use is INFICON XTC 751-001-G1.

RHEED is used to monitor the sample surface during growth. High energy electrons, usually 10~30keV and 15keV in my case, are diffracted by the sample surface, and create a diffraction pattern on a fluorescent screen, which indicates the surface crystalline structure. During the layer-by-layer growth, the intensity of RHEED pattern will oscillate, having a maximum when one layer is complete and a minimum when the surface is “roughest”. We use a commercial RHEED system from STAIB.

The TI-MBE system was put up all by myself.

Principles of MBE growth of Bi_2Se_3 on Si(111) surface

Bi_2Se_3 has a rhombohedral lattice, shown in Figure 1[4]. The lattice constants of the conventional cell are a = 4.14 Å and c = 28.9 Å. One conventional cell contains 15 atomic layers. Each layer is a triangular two dimensional (2D) lattice, and is composed purely of one element, Bi or Se. The 2D triangular lattices stack together in an A-B-C-A-B-C fashion (A,B,C represent the three possible sites in a hexagonal close-packed structure), and the composition has a five-layer period: Se-Bi-Se-Bi-Se, which is called a quintuple layer (QL). Within one QL, the bonding between atoms are covalent; however, the bonding between two neighboring QLs are due to Van de Waals interaction. Therefore, the bulk material is easy to cleave along the (0001) planes of this rhombohedral crystal, and the cleaved surfaces are usually atomically flat.

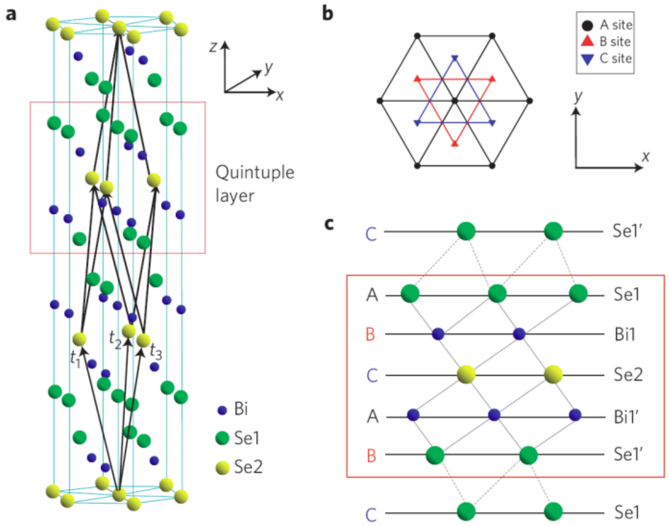


Fig. 1: Crystal structure of Bi_2Se_3. ***a.*** conventional cell; ***b.*** (0001) planes; ***c.*** layer composition

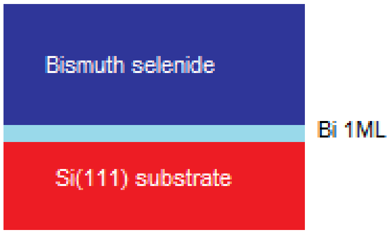


Fig. 2: Side view of the Si/Bi/Bi_2Se_3 structure.

The Si substrate has a diamond structure, and its (111) surface has a triangular lattice, like the lattice of Bi_2Se_3. The lattice constant of Si is 3.89 Å, thus manifesting a 6% mismatch from the Bi_2Se_3 (0001) plane.

The clean Si(111) surface usually forms a 7x7 reconstruction, which lowers the energy of the system and reduces dangling bonds in the Si atoms. But there are still residual dangling bonds, which tend to form Si-Se bonds and influence the MBE growth of Bi_2Se_3. So, there are literatures[5,6] suggesting a Bi spacing layer be deposited prior to the deposition Bi_2Se_3. The Bi spacing layer consists of only one atomic layer. Instead of keeping its own bulk lattice structure, the monolayer (ML) Bi forms a $\beta - \sqrt{3} \times \sqrt{3}$ reconstruction[7] on Si. Figure 2 shows a schematic side view of the Si/Bi/Bi_2Se_3 structure.

In a typical experiment, the substrate is a $2mm \times 5mm$ piece of highly n-doped Si. It is "flashed" several times to form 7x7 surface reconstruction in UHV with a base pressure of 1.2×10^{-10} Torr. During each flashing a high current of ~ 10 A is applied to the substrate for about three seconds; as a result, the substrate becomes bright whitish yellow, indicating the temperature is ~ 1400 K. The RHEED pattern of the Si should confirm the formation of the reconstruction.

After this, high purity Bi (99.999%) is deposited to the room-temperature substrate for a certain amount of time, which is calculated to be just enough for 1 ML.

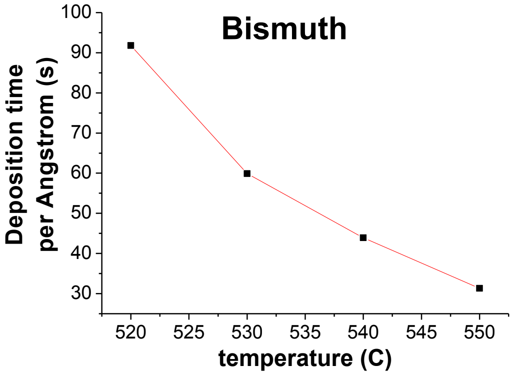
The substrate is further annealed to ~ 750K to form $\beta - \sqrt{3} \times \sqrt{3}$ reconstruction, which should be also confirmed by RHEED pattern. Then the substrate temperature is lowered to about 390K, and high purity Bi and Se (99.999%) are deposited together to the substrate, with the ratio Se:Bi about 10:1. As a result, Bi_2Se_3 will grow QL by QL, which can be seen from the RHEED intensity oscillation. The Se overpressure will minimize the amount of Se vacancies, and extra Se will not remain on the hot substrate.

STM measurement can by performed *in-situ*, to show the atomically flat surfaces of the thin film. And we have also done atomic force microscopy (AFM) measurements at ambient condition to view large scale topography.

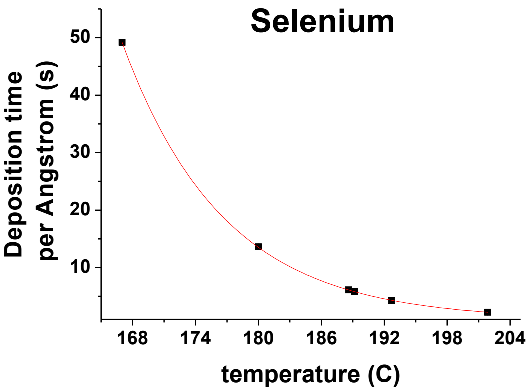
Results

Quartz crystal monitor

The deposition rates of the sources are temperature dependent, and are calibrated with quartz crystal monitor prior to any growth of Bi_2Se_3. Figure 3 (a) and (b) show the deposition rates of Bi and Se as functions of temperature, accordingly. In the experiment, the source temperature were decided to be $T_{Bi} = 540^0C$, and $T_{Se} = 195^0C$. The corresponding flux ratio of Se over Bi is 13:1.



(a)



(b)

Figure 3: deposition rates of (a) Bi and (b) Se.

RHEED

Typical RHEED patterns of Si(111) 7x7 reconstruction, Bi $\beta-\sqrt{3}\times\sqrt{3}$ reconstruction and Bi_2Se_3 taken in one complete growth are shown in Figure 4. The thickness of the films are around 20 QLs, and the average deposition rate is around 4 minutes per QL.

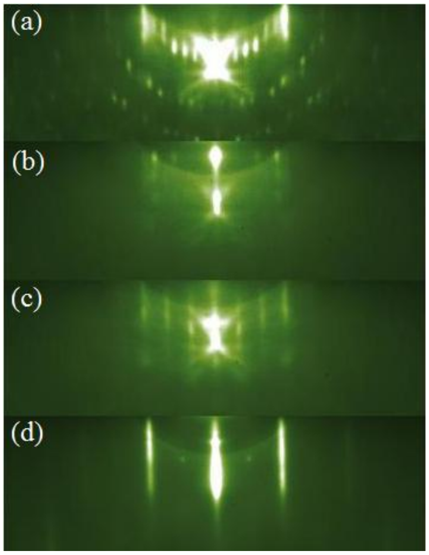


Figure 4: RHEED patterns taken in one growth. (a) Si(111) 7x7 (b) Bi 1ML (c) Bi $\beta-\sqrt{3}\times\sqrt{3}$ reconstruction (d) Bi_2Se_3

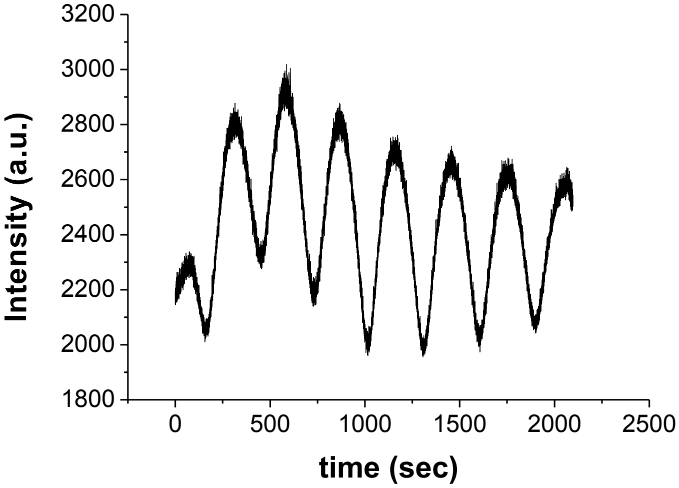


Fig. 5: RHEED intensity oscillation of a few QLs

The streak lines indicate the surface is flat. Fig. 4(a) agrees with other know Si(111) 7x7 RHEED patterns[8]. A comparison between (a) and (c) shows that the Bi $\beta-\sqrt{3}\times\sqrt{3}$ reconstruction really follows the crystal lattice of Si(111) surface; and the comparison between (a) and (d) confirms that the lattice mismatch between Bi and Si(111) is 6%.

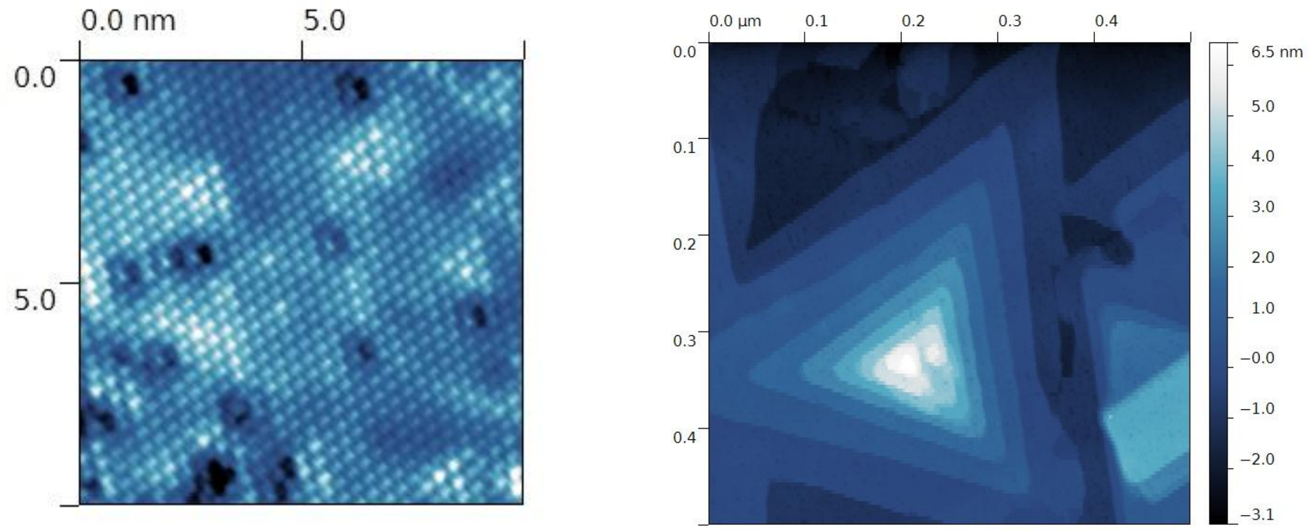
RHEED pattern intensity of a streak line is also measured during the growth, as shown in figure 5. The oscillation indicates that the growth is dominated by islands forming and coalescing[9], and that the growth is QL by QL.

STM

STM measurements and analysis are done by Chris Mann.

The Bi_2Se_3 can be transferred to a home-built STM *in-situ* and measured at low temperature. STM images with atomic resolution have been taken, as shown in figure 6(a). There are two kinds of defects in the epitaxial Bi_2Se_3 film, namely small dark circles and bright triangles. The dark circles are Se vacancies on the surface Se layer, while the bright triangles are the Se vacancies sandwiched between the two Bi layers of the top most QL.

In a larger range of about 1 micron, the topography of the surface is not completely flat, but has triangular wedding-cake-shaped islands, as shown in figure 6(b). The triangular shape agrees with the symmetry of the Bi_2Se_3 (0001) plane. Screw dislocations can be seen at the center of each triangular island. The screw dislocations may play an important role in the epitaxial growth, which need to be studied more in detail. Similar results have also been observed by other groups[10,11].

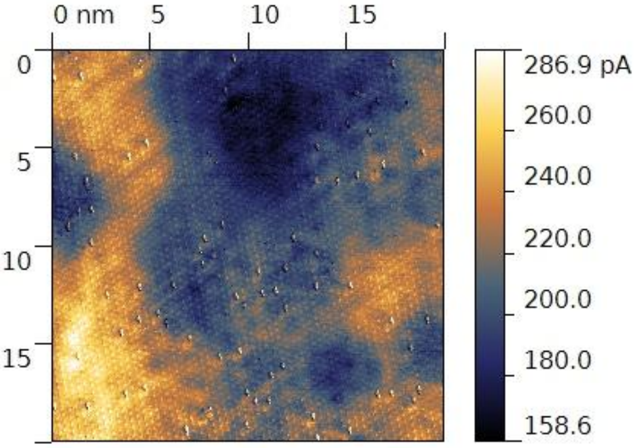


(a) (b)

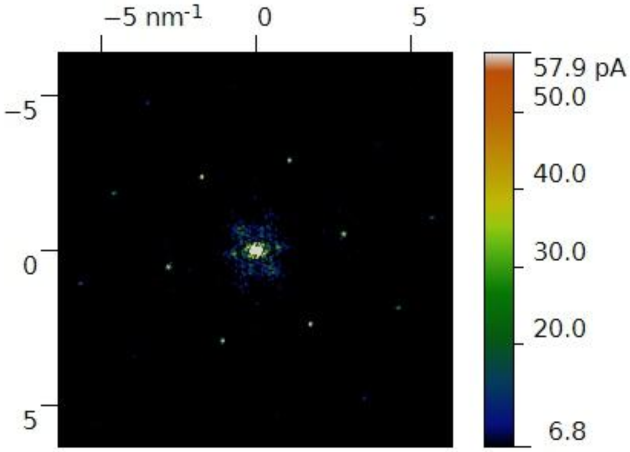
Figure 6: an STM images of Bi2Se3 epitaxial surface taken at 78K.

(a) Atomically flat surface. (b) A triangular wedding-cake-shaped island.

Spectroscopy measurements have also been done. A typical scanning tunneling spectroscopy (STS) and its Fourier transform are shown in figure 7. The Fourier transform image manifests a six-fold symmetry, resulting from the hexagonal 2D reciprocal lattice. The central bright cloud is from the scatterings that are not distinguishable at 78K. There are six arms extending outward from the center; these arms reflect the scattering from the Dirac cone of the surface state to the six bulk conduction band pockets[12]. The peripheral sharp bright dots come from the elastic scattering from the first Brillouin Zone (BZ) to the neighboring BZs, which reproduce the 2D reciprocal lattice. Spectroscopies at different bias voltages have been taken, from which the linear dispersion of the surface states can be extracted[13].



(a)



(b)

Figure 7 (a): STS taken at 120mV. (b) Corresponding Fourier

AFM

AFM images can show the topography of the samples in a larger scale. Figure 8 shows a $2\mu m \times 2\mu m$ region, in which the film is mostly of the same height, with sparse triangular wedding-cake shaped islands. The white spots are likely Bi clusters. Further experiments and thermal dynamics analysis are needed to fully understand the growth mechanism of Bi_2Se_3 and to improve the quality of the films.

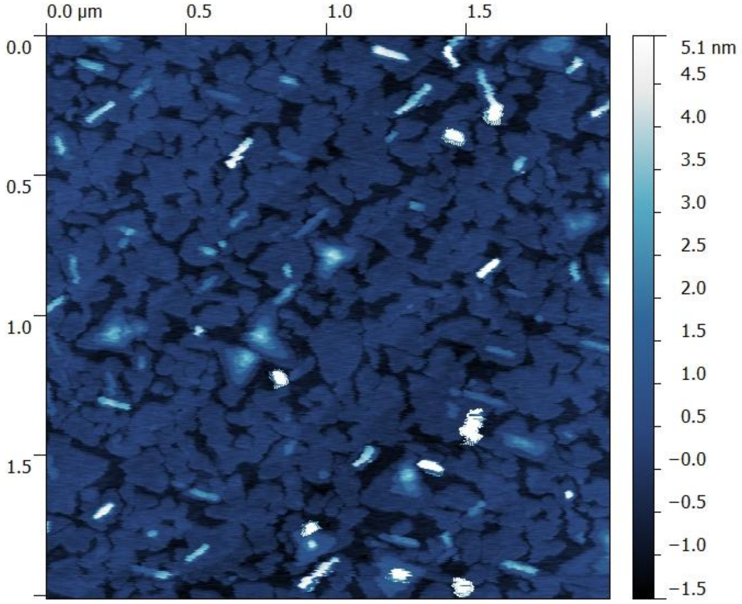


Figure 8: AFM image of a Bi2Se3 sample taken in ambient condition.

Conclusion

I have successfully grown atomically flat Bi_2Se_3 thin film using MBE method and the surface states have been observed. Further studies are required to understand the growth mechanism, and to improve the film quality. Transport measurements will be possible with more reliable samples. On the other hand, the screw dislocation formed during the growth is also an interesting topic, and it may unveil more information of the topological insulator.

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Vita

Yuxuan Chen was born in Xi'an, China, in 1986, and had been living there until admitted to Peking University, Beijing, China, in 2005, where he was awarded a Bachelor of Science degree in physics in 2009. In the same year, he entered the graduate school of the University of Texas at Austin, and joined the Ph.D. program of the department of physics.

Permanent email: cyuxuan@gmail.com

This thesis was typed by the author.