Interface structure of a topological insulator/superconductor heterostructure

Mei-Xiao Wang, Ping Li, Jin-Peng Xu, Zhi-Long Liu, Jian-Feng Ge, Guan-Yong Wang, Xiaojun Yang, Zhu-An Xu, Shuai-Hua Ji, CL Gao, Dong Qian, Weidong Luo, Canhua Liu and Jin-Feng Jia

1 Key Laboratory of Artificial Structures and Quantum Control, Department of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai 200240, People’s Republic of China
2 Department of Physics, Zhejiang University, Hangzhou 310027, People’s Republic of China
3 Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, People’s Republic of China
4 State Key Laboratory of Low-Dimensional Quantum Physics, Physics Department, Tsinghua University, Beijing 100084, People’s Republic of China
5 Institute of Natural Sciences, Shanghai Jiao Tong University, Shanghai 200240, People’s Republic of China

E-mail: canhualiu@sjtu.edu.cn and jfjia@sjtu.edu.cn

Received 8 September 2014, revised 14 November 2014
Accepted for publication 17 November 2014
Published 17 December 2014

Abstract

The construction of topological insulator/superconductor heterostructures attracts a lot of interest because of its potential to realize artificial topological superconductors hosting Majorana fermions. By means of molecular beam epitaxy, high-quality thin films of a topological insulator, Bi2Se3, can be grown on a superconductor substrate, 2H-NbSe2(0001), with an atomically smooth interface. To ascertain the atomic structure of the Bi2Se3/NbSe2 heterostructure, the initial growth stage was investigated with a scanning tunneling microscope (STM). In the growth process, we found that Bi atoms were first deposited to form a single Bi(110) bilayer, which is revealed to stand nearly freely on the NbSe2 surface and exhibits various moiré patterns. In the formation of the first quintuple layer of Bi2Se3 by co-depositing Bi and Se atoms, the Bi(110) bilayer transits to a BiSe interfacial layer, which effectively reduces the large lattice mismatch between Bi2Se3 and NbSe2. Based on atomic-resolution STM images and first-principles calculations, a NaCl-type structural model is proposed for the
BiSe interfacial layer, on which Bi$_2$Se$_3$ thin films grow well in a layer-by-layer mode.

Keywords: topological insulator, interface structure, scanning tunneling microscope

As a new state of matter, the topological insulator (TI) possesses a spin-momentum-locked gapless surface state band with a time reversal invariant [1–7]. Interplayed with magnetism and/or superconductivity, TIs can be used for potential applications in spintronics and/or quantum computing, and thus have triggered extensive research activities ever since their discovery several years ago [8–12]. It is theoretically predicted that introducing superconductivity to a TI’s surface state band via the proximity effect may create zero-energy quasiparticles bounded at Abrikosov vortex cores [13, 14], i.e., Majorana fermions (MFs), which are identical to their antiparticles and obey non-Abelian statistics for fault-tolerant quantum computing [8, 9]. This idea stimulated a great deal of experimental effort in search of MFs by constructing TI/superconductor (TI/SC) heterostructures, on several of which superconductivity has been manifested in the TI surfaces [15–18], and an indirect signature of MFs was revealed in the measurement of unconventional Josephson current on an Al/Bi$_2$Se$_3$/Al heterostructure [19]. So far, however, unambiguous evidence for the existence of MFs is still lacking in TI/SC heterostructures, although zero-energy end states, possible MFs, have been observed in some systems including hybrid superconductor-semiconductor nanowire devices and ferromagnetic iron atomic chains fabricated on a superconducting lead [20–24].

Visualizing individual Abrikosov vortices is a prerequisite for the detection and/or manipulation of a single MF in a TI/SC heterostructure, and it requires an atomically smooth superconducting surface in an STM measurement. Recently, we have succeeded in fabricating high-quality thin films of a TI, Bi$_2$Se$_3$, on a single crystal substrate of a SC, 2H-NbSe$_2$ (0001), by molecular beam epitaxy, and the coexistence of a topological surface state band and superconductivity has been verified [25–27]. It is worth noting, however, the lateral lattice mismatch between Bi$_2$Se$_3$ and NbSe$_2$ is as large as 20%. It is necessary to investigate the growth process of the Bi$_2$Se$_3$ thin films in detail to understand the formation of the high-quality heterostructure in spite of the large lattice mismatch. Moreover, discovery of the atomic structure of the TI/SC heterostructure, especially the atomic arrangement in the interface, is helpful for further theoretical study of the TI/SC-based artificial topological superconductors and the MFs therein.

In this work, we studied the initial growth stage of Bi$_2$Se$_3$ on NbSe$_2$ with STM, and obtained detailed information on the growth process. In particular, we reveal the existence of a BiSe interfacial layer between the Bi$_2$Se$_3$ thin films and the NbSe$_2$ substrate surface, and thus fully understand the growth of the high-quality Bi$_2$Se$_3$ thin films in spite of their large lateral lattice mismatch with the NbSe$_2$ substrate. Moreover, based on the high-resolution STM images, we proposed an atomic structural model for the BiSe interfacial layer, which is further refined by first-principles calculation. These results would be helpful for further quality improvement and doping-based property control of TI/SC heterostructures. Based on the atomic structural models proposed here, consequent theoretical studies on the properties of MFs residing in this system are anticipated.
Experiments were carried out in two connected ultra-high vacuum (UHV) chambers, one of which is equipped with a reflected high energy electron diffraction (RHEED) and the other with an STM. RHEED is used for in situ monitoring of the film growth. NbSe₂ single crystals were glued to highly doped silicon wafers and cleaved in UHV at room temperature after a thorough out-gas. In the growth of Bi₂Se₃ films, Bi atoms were firstly deposited alone onto the NbSe₂ surface at room temperature to form a single bilayer of Bi. After heating the NbSe₂ substrate to about 220 °C by a direct current flowing through the Si wafer, Se atoms were deposited onto the sample surface for 30 seconds, and Bi atoms were then co-deposited onto the surface. The evaporation rate of Se to Bi sources was around 10:1, and the typical growth rate of the Bi₂Se₃ thin films was about 0.3 quintuple layers (QL) per minute [28, 29]. Prepared samples were transferred to a cryogenic stage kept at 4.2 K for STM experiments.

NbSe₂ has a triple layered structure that consists of two hexagonal Se sheets with an intercalated Nb sheet (Se–Nb–Se) [30], as shown in the lower part of figure 1(a). Bi₂Se₃ has a quintuple layered structure consisting of Se–Bi–Se–Bi–Se hexagonal sheets. In both matters the triple layers or the quintuple layers are connected through van der Waals bonds. In-plane lattice constants of NbSe₂ and Bi₂Se₃ are 0.344 nm and 0.413 nm, respectively, giving a lattice mismatch of up to 20%. As the mismatch is too large for the direct epitaxial growth of Bi₂Se₃.
on NbSe₂, we first deposited Bi atoms onto the NbSe₂ surface and got a single Bi(110) bilayer, as revealed in STM images and shown in figure 1.

Figure 1(b) is a large-scale topographic STM image showing a Bi(110) terrace with a step height of 0.8 nm on the NbSe₂ surface. A zoomed-in STM image shown in figure 1(c) gives the atomic arrangement of the Bi(110) with one round spot corresponding to one Bi atom at the topmost layer. A red rectangle drawn in the figure indicates a unit cell of the Bi(110) with side lengths of 0.47 nm and 0.45 nm, both of which agree well with those of a Bi(110) surface reported previously [31].

In a free-standing Bi(110) bilayer structure, one unit cell contains two Bi atoms: one is at the corner that is a little higher than another one located very close to the center, as shown in figures 1(a) and 1(e). The center Bi atoms shift laterally along [001]Bi so that a zigzag chain forms along [110]Bi [31]. In our STM images shown in figure 1(c), no contrast difference between the corner and center atoms is visible. Instead, the outermost-layer Bi atoms exhibit a moiré pattern due to the lattice mismatch between the hexagonal NbSe₂ surface and the rectangular Bi(110) bilayer. In figure 1(e), the atomic model of Bi(110) bilayer is superimposed on that of NbSe₂ surface with an included angle of 6.5° between the [1120]sub and [001]Bi directions. One can see that some Bi atoms are located right above Se atoms while others are in between. The height of each Bi atom thus varies slightly depending on its location site with respect to the substrate Se atoms, resulting in the moiré pattern with contrast variation in STM images. Bi atomic sites located very close to substrate Se atoms are highlighted in the schematic illustration of the structural ball model in figure 1(d), giving a contrast variation that appears quite similar to that of the moiré pattern in STM image shown in figure 1(c). On some other Bi (110) domains of the same sample, we have observed other two types of moiré pattern with different contrast modulation, which can also be reproduced in the same way by highlighting the corresponding Bi location sites in the atomic structural ball models, as shown in figures 1(f) and (g). The only difference in the two cases is the included angles between [1120]sub and [001]Bi: one is about 0° while the other is 14.5°. It is worth noting that the STM images shown in the insets of figures 1(f) and (g) were taken in the same frame at the same bias voltage. Therefore, we can exclude the effects from the tip or bias dependence on the different contrast variation of the moiré patterns observed on different Bi(110) domains. Because of its incommensurate moiré pattern and small distortion in the atomic arrangement, we conclude that the Bi(110) bilayer lies nearly freely on the NbSe₂ surface with very weak coupling in between.

On the Bi(110) covered NbSe₂ surface kept at 220 °C, co-deposition of Bi and Se in a Se-rich atmosphere gives rise to a layer-by-layer growth of a Bi₂Se₃ film [25]. We intentionally controlled the amount of Bi adsorbate, so that the growth process of the Bi₂Se₃ film could be investigated in detail with STM. Figure 2(a) is a typical STM image taken on the sample prepared by co-depositing Bi and Se for 1.5 min on a 0.5 bilayer Bi(110)/NbSe₂ surface. Besides the 1st and 2nd QLs of the Bi₂Se₃ films and many Bi–Se alloy clusters randomly dispersed on the bare NbSe₂ surface, a totally new interfacial layer forms underneath the Bi₂Se₃ films while the previously prepared Bi(110) bilayer disappears. A line profile taken along the dotted line is presented in the lower part of figure 2(a), giving the specific thickness of each layer. The step heights of the interfacial layer and the 1st QL of Bi₂Se₃ are 0.7 nm and 1.6 nm, respectively, measured from the bare NbSe₂ surface. Figure 2(b) is an enlarged STM image, where one can see that the interfacial layer has a chain-like structure extending in four different directions indicated by the dashed lines, and the related angles between the four directions are carefully measured and presented thereon. While the angle of 60° should be due to the
hexagonal symmetry of the NbSe$_2$ substrate surface, the angle of 95° is believed to originate from the structural symmetry of the interfacial layer itself, as discovered below. It is very interesting to find that the included angle between $[1\bar{1}00]$ of the substrate and one of the chain direction was measured to be 47.5°, exactly half of 95°. This coincidence is the result of the atomic arrangement of the interfacial layer with respect to that of the substrate surface, which is discussed below. It is noted that we could no longer find the Bi(110) domain on the surface, indicating that the Bi(110) bilayer should have transited to the interfacial layer due to the co-deposition of Bi and Se.

STM images of the chain-like structure with atomic resolution were obtained at very low bias voltages, as shown in figures 2(c) and (d). Especially in figure 2(c), the bright spots are well distinguished and all have a round shape with a diameter of ~0.2 nm. Each of the round spots corresponds to one Bi or Se atom. We can figure out the top-most atomic arrangement by carefully measuring the relative positions of the round spots in the STM images. In contrast, in order to construct the atomic structural model for the interfacial layer, it is very helpful to note that single crystals of misfit layer compounds, (BiSe)$_{1.10}$(NbSe$_2$)$_m$, can be grown by chemical transport reactions when heating a stoichiometric combination of Bi, Se and Nb in a sealed tube [32–34]. Here, $m = 1, 2$. Such a (BiSe)$_{1.10}$(NbSe$_2$)$_m$ structure consists of an alternating sequence of a BiSe layer in a NaCl-type structure and $m$ slabs of Se–Nb–Se triple layers stacked along their c direction, and the two subsystems have their unit cells match perfectly along the b direction but not along the a direction. Based on the above discovery, we intuitively construct a
NaCl-type structural model for the interfacial layer and show it in figure 2(f) with the necessary lattice parameters obtained from the atomic-resolution STM images. Based on this NaCl-type structural model, our experimental results can be well understood. Firstly, the included angle between [010]BiSe and [100]BiSe is 95°, which explains well why we have an included angle of the same value between two chain directions found in figure 2(b). Secondly, it is easy to find that [110]_{sub} coincides with [010]_{BiSe}, since both of them have an included angle of 47.5° with [110]_{BiSe}, along which the BiSe chain extends. The lattice constant of the BiSe layer along [010]_{BiSe} is 0.593 nm, which is very close to that of the substrate surface along [110]_{sub}, i.e., 0.596 nm, as shown in figures 2(f) and (e), respectively. This means that the unit cells of the BiSe overlayer matches well with those of the substrate along [010]_{BiSe}, very similar to the case of (BiSe)_{1.10}(NbSe_{2})_{m} mentioned above. In this NaCl-type structural model, we put more Se atoms on the upper sheet and more Bi atoms on the lower one, since the substrate surface below the BiSe interfacial layer is terminated by a Se sheet, which should prefer to bond with more Bi atoms on the other side of the interface.

To refine the above NaCl-type structure of the BiSe interfacial layer and verify that the chain-like structures are energetically favorable, we performed first-principles calculations using projector augmented wave methods [35] with the Perdew–Burke–Ernzerhof generalized gradient approximation functional [35, 36] as implemented in the VASP codes [35, 37–39]. The calculated supercell contains three parts, a triple layer of the NbSe_{2} substrate, a bilayer of BiSe compound and a vacuum layer with thickness of 1.3 nm, as figure 3 shows. The BiSe bilayer is in a chain-like and strained NaCl-type structure with a compressive strain along the [110]_{BiSe} direction and a tensile strain in the perpendicular [110]_{BiSe} direction. The angle between the [010]_{BiSe} and [100]_{BiSe} directions is thus increased to 95° from the ideal value of 90°. The chain width is described by $m+n$ lines in the structural model, where $m$ and $n$ are the numbers of atomic lines along the chain direction in the bottom and top layers of the BiSe bilayer, respectively. For example, figure 3 shows a 6 + 5 lines model, in which 6 atomic lines consisting of 3 Bi and 3 Se lines are in the bottom layer while 5 atomic lines consisting of 3 Se and 2 Bi lines are shown in the top layer, as figure 3(b) clearly shows. The chain-like BiSe bilayer is put on the NbSe_{2} triple layer by coinciding [110]_{BiSe} and [110]_{sub} directions, along which the atomic separations are commensurate, as discovered in the above STM observations. In the
constructed supercell with this layout, the size of the NbSe$_2$ substrate is fixed when varying the $m+n$ lines of the BiSe bilayer, and each of the $m+n$ lines contains 10 Bi or Se atoms.

In the calculations, the energy cutoff is set to be 293 eV, and only the $\Gamma$-point in the Brillouin zone is used due to the large size of the supercell. Atoms in the two lower layers of the NbSe$_2$ triple layer are fixed while the others are all relaxed until the force acting on each atom is less than 0.5 eV·nm$^{-1}$. Several supercells with 4+4, 5+5 and 6+6 lines of the BiSe-bilayer chains are constructed, and their stability is judged by comparing the adsorption energy per BiSe unit defined as

$$\varepsilon_{BiSe}^a = \left(E_{cell} - n_{BiSe}\varepsilon_{BiSe} - n_{NbSe2}\varepsilon_{NbSe2}\right)/n_{BiSe}.$$  

In this equation, $E_{cell}$ is the supercell energy, $\varepsilon$ is the energy of the BiSe or NbSe$_2$ unit cell in their respective bulk phase, and $n$ is the corresponding unit number in the supercell. The calculated adsorption energy for the three structures mentioned above is 0.03, −0.10, and −0.08 eV per BiSe unit, respectively. Obviously, the 5+5 lines chain structure has the lowest negative adsorption energy, in good agreement with the above STM images, in which 5 lines of atoms are observed on the top-most layer of each BiSe chain.

However, the atomic geometry of the 5+5 lines chain becomes disordered after relaxation, especially in the lower layer of the BiSe bilayer, and thus deviates remarkably from the STM observations. Therefore, we added an extra Se line at the lower layer to form a 6+5 lines chain structure, as figure 3 shows. The extra Se line is indicated with an arrow in figure 3(a). The calculated stable structure of the 6+5 lines chain structure after relaxation is shown in figure 4, in which one can see that, except for the extra Se line, other Bi and Se atoms form a NaCl-type structure with bond angles varying from 94° to 101° in the top BiSe layer, roughly in agreement with the STM observations. Moreover, the mean distance between the bottom BiSe layer and the top layer of the NbSe$_2$ substrate is larger than 0.32 nm, indicating that the BiSe bilayer is a nearly-free-standing layer.

On the BiSe bilayer, high-quality Bi$_2$Se$_3$ thin films start to grow in the layer-by-layer mode, as already seen in figure 2. Increasing the co-deposition time of Bi and Se atoms results in larger terraces of both the BiSe bilayers and the 1st Bi$_2$Se$_3$ QLs, as revealed in STM images shown in figure 5(a). The BiSe interfacial layer has very straight edges due to its chain-like geography in structure, while the 1st QL of Bi$_2$Se$_3$ has irregular-shaped edges.
part of the STM image and performed a differential transform on it. We found that the surface of the 1st QL of Bi$_2$Se$_3$ exhibits a striped modulation extending in the same direction as that of the BiSe chains beneath it, as shown in figure 5(b). The striped modulation on the 1st QL of Bi$_2$Se$_3$ is obviously due to its interplay with the BiSe bilayer underneath. Such a modulation is much more clearly visible in an STM image taken at a sample bias of $V_s = 1$ V, as shown in figure 5(c). The modulation is so strong that the surface appears to be consisting of an array of nanowires with diameters of 2.5–3.7 nm. In figure 5(d), a zoomed-in STM image taken at $V_s = 0.3$ V exhibits a hexagonal pattern with an periodicity of 0.42 nm, which agrees very well with the lattice constant (0.413 nm) of a Bi$_2$Se$_3$ surface. It is found that the [1120] lattice orientation of the Bi$_2$Se$_3$ films coincides with the BiSe chain direction. In this direction, the Se–Se atom distances are 0.42 nm and 0.40 nm in the Bi$_2$Se$_3$ layer and the BiSe layer, respectively, giving a lattice mismatch of only 5%. It is seen now that the lattice mismatch between Bi$_2$Se$_3$ and NbSe$_2$ is efficiently reduced by the BiSe interfacial layer. Further co-deposition of Bi and Se leads to high-quality layer-by-layer growth of Bi$_2$Se$_3$, as shown in figures 5(e) and (f).

Figure 5. (a) Topographic STM image taken at the initial growth stage of Bi$_2$Se$_3$ with $V_s = 2.00$ V and $I = 100$ pA. (b) Derivative STM image taken from the area indicated by the dashed square in (a), showing the stripe modulation on Bi$_2$Se$_3$ along the chain direction of the BiSe interfacial layer. (c) and (d) STM images taken on the 1st QL of Bi$_2$Se$_3$ with $V_s = 1.00$ V, $I = 100$ pA and $V_s = 285$ mV, $I = 150$ pA, respectively. (e) and (f) Topographic STM images in large scale taken on different growth stages of Bi$_2$Se$_3$ with $V_s = 2.00$ V, $I = 100$ pA and $V_s = 1.00$ V, $I = 120$ pA, respectively.
In summary, we investigated the initial growth stage of Bi$_2$Se$_3$ thin films on a NbSe$_2$ substrate in detail. A pre-prepared Bi(110) bilayer was revealed to be a nearly-free-standing layer on the NbSe$_2$ substrate. After reacting with Se, it transits to a BiSe layer interfacially existing between the Bi$_2$Se$_3$ thin films and the NbSe$_2$ surface. Based on atomic-resolution STM images and first-principles calculations, we proposed a NaCl-type structural model for the BiSe interfacial layer, which efficiently reduces the lattice mismatch between the Bi$_2$Se$_3$ thin films and the NbSe$_2$ surface. This work provides useful information for the construction of a Bi$_2$Se$_3$/NbSe$_2$ heterostructure, which is one of the promising candidate materials for topological superconductors and thus can be used in searching for Majorana fermions bound at Abrikosov vortex cores.

Acknowledgments

This work is supported by National Basic Research Program of China (grant nos. 2012CB927401, 2011CB922200, 2013CB921902, and no. 2011CB921902), NSFC (grant nos. 11174199, 11134008, 11474197, 11374206, 11227404, 91021002, 91221302, and 11274228), Open Research Fund Program of the State Key Laboratory of Low-Dimensional Quantum Physics, and Shanghai Committee of Science and Technology (12JC140530 and 13QH1401500). CLG acknowledges support from the Shu Guang project, which is supported by the Shanghai Municipal Education Commission and Shanghai Education Development Foundation. DQ acknowledges support from the Top-notch Young Talents Program and the Program for Professor of Special Appointment (Eastern Scholar). Computations were performed at the Center for HPC, Shanghai Jiao Tong University.

References

[1] Qi X-L and Zhang S-C 2010 Phys. Today 63 33
[2] Hasan M Z and Kane C L 2010 Rev. Mod. Phys. 82 3045
[3] Moore J E 2009 Nat. Phys. 5 378
[4] Fu L and Kane C L 2007 Phys. Rev. B 76 045302
[5] Hsieh D et al 2008 Nature 452 970
[6] Xia Y et al 2009 Nat. Phys. 5 398
[7] Chen Y L et al 2009 Science 178 325
[8] Nayak C et al 2008 Mod. Phys. Rev. 80 1083
[9] Kitaev A Y 2003 Ann. Phys. 303 2
[10] Tao J C Y and Kane C L 2010 Phys. Rev. Lett. 104 046401
[11] Song Y R et al 2012 Appl. Phys. Lett. 100 242403
[12] Li H et al 2012 Appl. Phys. Lett. 101 072406
[13] Fu L and Kane C L 2008 Phys. Rev. Lett. 100 096407
[14] Hosur P et al 2011 Phys. Rev. Lett. 107 097001
[15] Sacépé B 2011 et al Nat. Commun. 2 575
[16] Zhang D et al 2011 Phys. Rev. B 84 165120
[17] Yang F et al 2012 Phys. Rev. B 86 134504
[18] Wang E et al 2013 Nat. Phys. 9 621
[19] Williams J R et al 2012 Phys. Rev. Lett. 109 056803
[20] Mourik V et al 2012 Science 336 1003
[21] Rokhinson L P et al 2012 Nat. Phys. 8 795
[22] Das A et al 2012 Nat. Phys. 8 887
[23] Deng M T et al 2012 Nano Lett. 12 6414
[24] Nadj-Perge S et al 2014 Science 346 602
[25] Wang M-X et al 2012 Science 336 52
[26] Xu J-P et al 2014 Phys. Rev. Lett. 112 217001
[27] Xu J-P et al 2013 Majorana mode in vortex core of Bi$_2$Te$_3$/NbSe$_2$ topological insulator-superconductor heterostructure arXiv: 1312.7110
[28] Li Y Y et al 2010 Adv. Mater. 22 4002
[29] Zhang Y et al 2010 Nat. Phys. 6 584
[30] Meerschaut A and Deudon C 2001 Mater. Res. Bull. 36 1721
[31] Hofmann P 2006 Prog. Surf. Sci. 81 191
[32] Nadar A et al 1997 Solid State Commun. 101 149
[33] Zhou W Y et al 1992 Mater. Res. Bull. 27 563
[34] Heideman C et al 2008 J. Solid State Chem. 181 1701
[35] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[36] Blöchl P E 1994 Phys. Rev. B 50 17953
[37] Perdew J P et al 1996 Phys. Rev. Lett. 77 3865
[38] Kresse G and Hafner J 1993 Phys. Rev. B 48 13115
[39] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169