Epitaxial growth of bilayer Bi(110) on two-dimensional ferromagnetic Fe₃GeTe₂

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Abstract
Heterostructures of two-dimensional (2D) layered materials with selective compositions play an important role in creating novel functionalities. Effective interface coupling between 2D ferromagnet and electronic materials would enable the generation of exotic physical phenomena caused by intrinsic symmetry breaking and proximity effect at interfaces. Here, epitaxial growth of bilayer Bi(110) on 2D ferromagnetic Fe₃GeTe₂ (FGT) with large magnetic anisotropy has been reported. Bilayer Bi(110) islands are found to extend along fixed lattice directions of FGT. The six preferred orientations could be divided into two groups of three-fold symmetry axes with the difference approximately to 26°. Moreover, dI/dV measurements confirm the existence of interface coupling between bilayer Bi(110) and FGT. A variation of the energy gap at the edges of bilayer Bi(110) is also observed which is modulated by the interface coupling strengths associated with its buckled atomic structure. This system provides a good platform for further study of the exotic electronic properties of epitaxial Bi(110) on 2D ferromagnetic substrate and promotes potential applications in the field of spin devices.

Keywords: Bi(110) film, FGT ferromagnet, electronic structure, STM, interface coupling, heterostructures

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)

1. Introduction

Bismuth, as the last element of the nitrogen group, has become a research hotspot in recent decades, owing to its dramatically exotic physical properties and chemical properties, and its widely developed applications in many fields [1–3]. For example, bismuth is a promising anode material for sodium-ion batteries due to its high capacity and suitable operating potential. The electrochemical reduction of carbon dioxide has the potential to directly convert renewable electricity into valuable chemical raw materials or fuels, thereby closing the anthropogenic carbon cycle, in which bismuth as a highly efficient electrocatalyst for carbon dioxide reduction reaction plays an important role in the field of catalysis [4–10]. Bismuth can also be used as a strain-independent infrared reducer optoelectronic material for biophotonics [11]. Semimetal bismuth is imperative to condensed matter physics due to its exotic intrinsic properties such as high atomic number, long Fermi wavelength as well as strong intrinsic spin-orbital coupling (SOC) [12–16], which endow bismuth great potential in the field of the electronic and spintronic devices.

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Figure 1. (a) The top-view crystal structure of FGT. (b) The side-view crystal structure of FGT. (c) X-ray diffraction pattern obtained from the cleaved plane of an FGT crystal at room temperature. The red line is the standard location and intensity, and the blue line is the measured data. The image of a representative single crystal is shown in the inset. (d) The Raman spectrum of grown FGT collected at room temperature. The insets represent the in-plane mode of E_{1g} and the out-of-plane modes of A_{1g} and A_{2g}. (e) The SEM image of FGT nanosheet on conductive substrate. (f)–(h) Respectively show EDS elemental mapping images of Fe, Ge and Te atoms, corresponding to rectangle in (e).

Inspired by the discovery of graphene [17], the investigations into two-dimensional (2D) materials have undergone a burgeoning growth [18–23]. The electronic properties of ultrathin films are completely different from those of their bulk counterparts owing to size effects and/or structure changes. These effects are particularly pronounced for Bi thin films, because their special electronic properties are balanced between metals and semiconductors. Stacking different layered 2D crystals into heterostructure opens an opportunity to create new materials and control their electronic properties, offering unprecedented freedom in combining different materials as well as providing novel physics. In recent years, ultra-thin Bi films have been successfully grown on various metallic and semiconducting substrates, in the form of either Bi(110) or Bi(111) depended on the growth conditions and coverages [24–28]. Bilayer Bi(111) films, also known as bismuthene, have become a research hotspot in recent years as a high-temperature quantum spin Hall material [29–31]. Metal to semiconductor transition on ultra-thin Bi(110) film has been reported due to its edge reconstructions, in which a large energy gap of 0.4 eV makes it appeal in practical applications as electronic devices in nano-scale [16]. Topological properties have also been identified on Bi(110) films grown on highly oriented pyrolytic graphite (HOPG) substrate, which exhibit sensitivity towards the interaction between the film and its substrate [32]. Meanwhile, it has been recognized that the interface coupling between the Bi(110) film and its substrate could influence the electronic properties of the system through determining the atomic structure, interface charge transfer, orbital hybridization and proximity effect, as exemplified by the unusual superconducting proximity effect on Bi(110) grown on NbSe2 substrate [33]. Thus, growing ultra-thin Bi films on functional substrates and engineering the interface coupling would benefit for searching exotic physical phenomena and potential applications.

The recent discovery of intrinsic 2D ferromagnetism in layered materials opens up unprecedented opportunities for exotic phenomena and device applications [34–39]. Among these, 2D ferromagnetic materials, Fe3GeTe2 (FGT) is significantly promising due to high Curie temperature (Tc) in bulk, which could be tuned to room temperature by using ion gating in the 2D form [35]. Considering the itinerant ferromagnetic property of FGT, the large magnetic anisotropy and strong SOC suppress thermal fluctuations, leading to long-range magnetic order. Moreover, as magnetism is based on strong short-range correlations between electron spin and orbital degrees of freedom that are inherently changed at the interfaces [40], the interface coupling between 2D ferromagnetic materials and epitaxially grown thin films could not only modify its magnetic properties but also the physical properties of adjacent nonmagnetic layers, especially for those materials with strong SOC including Bi ultra-thin films.

Based on the above-mentioned motivations, in this work we have grown sub-monolayer bilayer Bi(110) islands on FGT substrate which is a robust 2D ferromagnet with strong magnetic anisotropy. Through scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS) studies, it is found that the islands with different diameters appear randomly over the surface. By comparing these bilayer Bi(110) islands atomic lattices, it is determined that the islands extend along six preferred orientations approximately ±13° from the [001] direction of the FGT(001) growth substrate. Importantly, the dI/dV spectra reveals that effective interface couplings exist in both the
Figure 2. STM images of different Bi coverage on FGT surface. (a) Bi clusters, (b) growth Bi islands, (c) larger Bi islands. (d)–(f) Show the corresponding line-scan profiles taken along the red dashed arrows in (a) to (c), respectively.

2. Experimental detail

High-quality single crystals of FGT were grown by using chemical transport method with iodine as the transport agent according to reference [34]. High-purity Fe (99.99%), Ge (99.99%), and Te (99.99%), in a stoichiometric ratio of 3:1:2 with iodine as the transport agent were sealed in an evacuated quartz tube. Powder x-ray diffraction (XRD, PANalytical X9 PertPro x-ray diffractometer using Cu $K\alpha$ radiation) was performed to investigate the structure of FGT samples. Raman measurements at room temperature were performed on an inVia Reflex Raman spectrometer with a laser at 532 nm. The surface morphologies of the GeH samples were investigated using scanning electron microscopy (SEM, JEOL JSM-7500FA). Besides, the elemental analysis was performed on an energy dispersive x-ray spectroscopy (EDS, OXFORD INCA X-ACT).

STM and STS measurements were performed using a low-temperature STM system (STM1500, Unisoku Co.) under ultrahigh vacuum at 4.2 K. An FGT single crystal was cleaved with a Scotch tape to obtain a shiny mirror-like surface under vacuum of better than $5.0 \times 10^{-10}$ Torr. And then, high-purity Bi (99.99%) was deposited onto the surface of FGT at room temperature using a standard Knudsen cell. All measurements were performed at 4.2 K. All the STM images were obtained in constant current mode. The STS differential conductance ($dI/dV$) was obtained with lock-in detection by applying modulation to the tunnel at 613 Hz. All the STM images were analyzed by WSxM software [41].

3. Results and discussion

FGT is a van der Waals (vdW) metallic ferromagnet with the space group $P6_3/mmc$ [42, 43]. Figures 1(a) and (b) show the top-view and side-view crystal structures of FGT, respectively. FGT monolayer consists of covalently bonded Fe$_3$Ge$_2$ layer and Te layers above and below the Fe$_3$Ge$_2$ layer. In an FeGe$_3$ layer, there are two inequivalent Wyckoff Fe sites denoted as Fe$_1$ and Fe$_2$. Due to the weak vdW bonding, FGT flakes easily exfoliated from the bulk crystals have the plane surfaces parallel to the Fe$_3$Ge$_2$ layers. Figure 1(c) shows the x-ray pattern of grown FGT crystal, in which all peaks can be indexed to the space group $P6_3/mmc$. It is clear that the peaks only show the $c$ axis normal with exclusively 00l diffraction, indicating that the grown FGT is a high-quality single crystal. The as-grown single crystals are prepared with lateral dimensions up to several millimeters by using chemical transport method (inset figure 1(c)). The Raman spectrum of FGT sample in figure 1(d) shows three phonon peaks at 122.21 cm$^{-1}$ ($E_{1g}^{\perp}$ vibrational mode), 143.27 cm$^{-1}$ ($A_{1g}^{\perp}$ vibrational mode) and 268.85 cm$^{-1}$ ($A_{2g}^{\perp}$ vibrational mode) at room temperature. These three Raman modes are illustrated in the insets of figure 1(d). The Raman mode of $E_{1g}^{\perp}$ represents the in-plane vibration including all atoms, while the Raman modes of $A_{1g}^{\perp}$ and $A_{2g}^{\perp}$ respectively show Te and Fe atoms vibration.
Figure 3. (a) Large scale STM image of the bilayer Bi(110) island on FGT surface. (b) The atomic resolved STM topography of a bilayer Bi(110) island terrace from the blue square in (a). (c) The atomic resolved STM topography of a neighboring FGT(001) substrate from the green square in (a), where the angle between short length of Bi crystal lattice (blue dashed arrow line) and the Te atom chains of FGT surface (black solid arrow line) is 73°. (d) Schematic illustration of side- and top-views of a bilayer Bi(110) crystal structure. (e) Side view of bilayer Bi(110) stacked on FGT substrate. (f) The schematic preferred orientation of bilayer Bi(110) islands grown on FGT substrate.

In our experiment, FGT is used as the substrate to support a layer-by-layer growth of Bi(110) islands. The schematic illustration of our experimental setup is illustrated in figure S1(a) (https://stacks.iop.org/JPCM/34/074003/mmedia), in which Bi atoms are evaporated from a standard Knudsen cell onto an FGT surface at room temperature. The coverage of Bi on the surface of FTG is controlled by the depositing time at a constant Bi flux. The samples are then cooled to 4.2 K for STM and STS measurements (detailed in the experimental section). Due to Bi is a heavy metal atom with strong SOC, remarkable interplay between spin-spin and spin-orbital at the interface with FGT substrate is expected to happen as illustrated in figure S1(b), which is highly desired in developing new spintronic devices.

The evolution of the topographies of sub-monolayer Bi on FGT substrate are characterized by low-temperature STM system. As shown in figure 2(a), at the initial stage of growth, the Bi clusters randomly distribute on the FGT substrate (STM images of bare FGT substrate are shown in figure S2). The corresponding height profile of several Bi clusters is shown in figure 2(d). With the coverage increasing, flat Bi islands appear on the surface as shown in figure 2(b), whose size further increases in the in-plane directions to several tens of nanometers at even higher Bi coverage as shown in figure 2(c). Those isolated Bi islands with different sizes show an identical thickness. As shown in the height profiles in figures 2(e) and (f), the apparent heights are around 0.69 nm which is consistent with bilayer Bi(110) [16, 45]. In fact, according to pervious research the freestanding ultra-thin Bi(110) islands prefer to form a bilayer structure due to their dangling bonds. As the outermost shell electron configuration of Bi is 6s^26p^3, each atom in the bulk Bi forms three σ bonds with its nearest neighbors. At the low coverage, a ladder structure with dangling bonds is formed, thus preferring to adopt the bilayer (or even monolayer) stacking mode in freestanding ultra-thin Bi(110) islands [15, 32].

Figure 3(a) shows the representative STM image of the bilayer Bi islands on FGT substrate in the sub-monolayer regime. The atomically resolved STM image of Bi(110) thin film is shown in figure 3(b), in which a rectangle with crystal lattice constants of 4.73 Å × 4.52 Å along the long edge as indicated by the arrow line. Meanwhile, it is found that almost all the angles between these sharp long edges and short edges are 145°. Thus, the edges are determined to terminate along the unit cell direction (b direction for the long edges) or the diagonal direction of the unit cell. The top-view...
Figure 4. (a) Typical STM image of Bi(110) island. (b) Close-up STM image showing the reconstructions at the edge. (c) Line profile along the edge (blue solid line) in panel (b). (d) The typical $dI/dV$ spectra taken at the positions indicated by the color dots, indicated in (a). (e) 2D plot of tunnelling spectra measured along the white dashed arrow line in (a).

and side-view crystal structures of Bi(110) are illustrated in figure 3(d). Each bilayer Bi(110) contains two bonded Bi atom sublayers forming a layered structures normal to its plane. The surface atoms form a rectangular unit cell with the crystal lattice constants of 4.75 Å × 4.54 Å, consistent with previously mentioned STM atomic structure. Moreover, the islands extend along the shorter side of the unit cell of Bi(110), similar phenomenon has been observed in Bi(110) islands grown on Si(111) $\sqrt{3} \times \sqrt{3}$-B substrate [46]. Figure 3(c) illustrates the detailed atomic network of FGT surface, clearly showing that the top Te-terminal surface has a hexagonal lattice structure (4.00 Å). By comparing these Bi(110) atomic lattices with the structure of a neighboring FGT(001) growth substrate, the angle between the shorter length of Bi(110) lattice and the exposed Te-terminal surface in FGT is 73° (figure 3(c)). Figure 3(e) exhibits one of stacking configurations between a bilayer Bi(110) and FGT(001) substrate. By comparing tremendous Bi(110) structures with the atomic lattice of the neighboring FGT(001) growth substrate, it is found that the Bi(110) islands extend along six preferred orientations, as shown in figure 3(f). It can be seen that these six preferred orientations could be divided into two groups of three-fold symmetry axes with the difference approximately to 26°. The similar phenomenon has also been reported at Bi(110) on Si(111) $\sqrt{3} \times \sqrt{3}$-B substrate [46, 47]. The fixed directions of epitaxially grown bilayer Bi(110) islands imply the existence of necessary interface coupling between bilayer Bi(110) islands and FGT substrate.

Effective interface coupling on the electronic structures between Bi(110) and FGT is also confirmed in the STM/STS characterizations. Figure 4(a) shows the typical STM image of a bilayer Bi(110) island. It is found that the island has a ribbon-shape with a flat terrace in the middle and hump-like reconstructions along the long edges. Figure 4(b) shows the enlarged STM image at the edge to emphasize the subtle reconstructions. A line profile of hump-like superstructures at the edge of Bi (110) island (blue line in figure 4(b)) is illustrated in figure 4(c), which is a $4 \times 1$ reconstruction. This phenomenon is similar to the Bi(110) island grown on HOPG substrate caused by strain energy relaxation [16]. Figure 4(d) exhibits typical $dI/dV$ curves measured at different positions, as indicated in figure 4(a). The density of states near the Fermi level of FGT is higher than that of bilayer Bi(110) island and edges, which is consistent to the semimetal properties of bismuth. In addition, several features of Bi island and FGT substrate share similarities in their $dI/dV$ curves, indicating effective interface coupling in their electronic structures. For example, a prominent peak at a sample bias $-60$ mV, that originates from Fe 3d orbitals [39], is identified on both Bi island and FGT. Moreover, for the two edges further suppression of the density of states near the Fermi level is identified, which agrees with the gap opening behavior due to structure reconstruction. Interestingly, it is found that the gaps at the two edges show an apparent shift as can been seen more clearly in the line map shown in figure 4(e) (along the white dashed arrow line in figure 4(a)). As the position of the gap does not vary along the long edges (figures S3 and S4), this shift of the gap is very likely caused by the different interface coupling strength with FGT at the two edges, which origins from the buckled atomic structure (figure 3(d)). A similar effect of the buckled
atomic structure on the interface coupling has been observed on bilayer Bi(111). The variation of the interface coupling caused by buckled atomic structure of bilayer Bi(110), thus, not only demonstrates its existence but also suggests the feasibility of engineering the electronic structure of this system by adjusting its atomic structure.

4. Conclusion

In summary, atomically flat bilayer Bi(110) islands have been successfully grown on 2D ferromagnetic FGT substrate. The structural and electronic properties of this system are investigated by low-temperature STM-STS experiments. In the STM and STS studies, the effective interface coupling between bilayer Bi(110) and FGT is demonstrated through characterizing their atomic structures and local electronic structures. We observe that the islands have six preferred orientations approximately ±13° from the [100] direction of the FGT(001) growth substrate. In addition, a 4 × 1 reconstruction is observed on the long edges of bilayer Bi(110), whose energy gap is sensitive to the atomic buckled structure. The experimental realization of effective interface coupling between 2D ferromagnet and bismuth ultra-thin structures would promote the insights into the understanding of heterostructure in this system and the possible applications of spintronic devices.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

References

[1] Zhou J et al 2019 Adv. Mater. 31 1807874
[2] Fan J et al 2021 Adv. Mater. 33 2100910
[3] Lu L et al 2018 Laser Photonics Rev. 12 1700221
[4] Han N, Wang Y, Yang H, Deng J, Wu J, Li Y and Li Y 2018 Nat. Commun. 9 1320
[5] Yang F et al 2020 Nat. Commun. 11 1088
[6] Gong Q et al 2019 Nat. Commun. 10 2807
[7] Yang H et al 2018 Adv. Energy Mater. 8 1801536
[8] Zhang E et al 2019 J. Am. Chem. Soc. 141 16569
[9] Zhang X, Sun X, Guo S-X, Bond A M and Zhang J 2019 Energy Environ. Sci. 12 1334
[10] Yu X, Fautrelle Y, Ren Z and Li X 2015 Mater. Lett. 161 144
[11] Karacay Shiraz A and Yazdani-Panah Goharrizi A 2020 Phys. Status Solidi b 257 1900408
[12] Issi J-P 1979 Aust. J. Phys. 32 585
[13] Li L, Checkelsky J G, Hor Y S, Uher C, Hebard A F, Cava R J and Ong N P 2008 Science 321 547
[14] Murakami S 2006 Phys. Rev. Lett. 97 236805
[15] Hofmann P 2006 Prog. Surf. Sci. 81 191
[16] Sun J-T, Huang W, Song L, Gao H-J, Feng Y P and Wee A T S 2012 Phys. Rev. Lett. 109 246804
[17] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Science 306 666
[18] Zhang Z, Chen P, Duan X, Zang K, Luo J and Duan X 2017 Science 357 788
[19] Liu Z et al 2013 Nat. Nanotechnol. 8 119
[20] Stoller M D, Park S, Zhu Y, An J and Ruoff R S 2008 Nano Lett. 8 3498
[21] Yuan K, Zhuang X, Fu H, Brunklau G, Forster M, Chen Y, Feng X and Scherf U 2016 Angew. Chem., Int. Ed. 55 6858
[22] Yuan K et al 2015 Adv. Mater. 27 6714
[23] Sierra J F, Fabian J, Kawakami R K, Roche S and Valenzuela S O 2021 Nat. Nanotechnol. 16 856
[24] Nagao T et al 2004 Phys. Rev. Lett. 93 105501
[25] Matsushima H, Lin S-W, Morin S and Magnussen O M 2016 Faraday Discuss. 193 171
[26] Yagimina S, Nagao T, Sadowski J T, Saito M, Naqoaka K, Fujikawa Y, Sakurai T and Nakayama T 2007 Surf. Sci. 601 3593
[27] Peng L, Xian J-T, Tang P, Rubio A, Zhang S-C, Zhang W and Fu Y-S 2018 Phys. Rev. B 98 245108
[28] Kowalczuk P J, Mahapatra O, McCarthy D N, Kozlowski W, Klusek Z and Brown S A 2011 Surf. Sci. 605 659
[29] Drozdov I K, Alexandradinata A, Jeon S, Nadj-Perge S, Ji H, Cava R J, Andrei Bernevig B and Yazdani A 2014 Nat. Phys. 10 664
[30] Kim S H, Jin K H, Park J, Kim J S, Jhi S H and Yeom H W 2016 Sci. Rep. 6 33193
[31] Sun H-H et al 2017 Nano Lett. 17 3035
[32] Lu Y et al 2015 Nano Lett. 15 80
[33] Peng L, Qiao J, Xian J J, Pan Y, Ji W, Zhang W and Fu Y S 2019 ACS Nano 13 1885
[34] Chen B, Yang J, Wang H, Imai M, Ohta H, Michioka C, Yoshimura K and Fang M 2013 J. Phys. Soc. Japan 82 124711
[35] Deng Y et al 2018 Nature 563 94
[36] Huang B et al 2018 Nat. Nanotechnol. 13 544
[37] Gong C and Zhang X 2019 Science 363 eaav4450
[38] Zhang Y et al 2018 Sci. Adv. 4 eaao6791
[39] Zhao M et al 2021 Nano Lett. 21 6117
[40] Hellman F et al 2017 Rev. Mod. Phys. 89 052006
[41] Horcas I, Fernández R, Gómez-Rodríguez J M, Colchero J, Gómez-Herrero J and Baro A M 2007 Rev. Sci. Instrum. 78 013705
[42] You Y et al 2019 Phys. Rev. B 100 134441
[43] Ke J et al 2020 J. Phys.: Condens. Matter 32 405805
[44] Kong X, Berlijn T and Liang L 2021 Adv. Electron. Mater. 7 2001159
[45] Dong X et al 2019 J. Phys. Chem. C 123 13637
[46] Kokubo I, Yoshiike Y, Nakatsuji K and Hirayama H 2015 Phys. Rev. B 91 075429
[47] Nagase K, Kokubo I, Yamanaki S, Nakatsuji K and Hirayama H 2018 Phys. Rev. B 97 195418

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