Topological quantum weak antilocalization limit and anomalous Hall effect in semimagnetic Bi$_{2-x}$Cr$_x$Se$_3$/Bi$_2$Se$_3$–yTe$_y$ heterostructure

Moothi Kanagaraj ©, Sun Yizhe¹, Jai Ning¹, Yafei Zhao¹, Jian Tu¹, Wenqin Zou¹,² and Liang He¹,³,４

¹ School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, People’s Republic of China
² National Lab of Solid State Microstructures, Department of Physics, Nanjing University, Nanjing 210093, People’s Republic of China
³ Yook-Nanjing Joint Center for Spintronics and Nano Engineering (YNJC), School of Electronics Science and Engineering, Nanjing University, Nanjing 210093, People’s Republic of China
⁴ Authors to whom any correspondence should be addressed.

E-mail: wqzou@nju.edu.cn and heliang@nju.edu.cn

Keywords: magnetic topological insulator, epitaxial growth, proximity effect, quantum anomalous Hall effect, weak antilocalization

Abstract

Magnetic topological insulator hosts both a non-trivial surface band and quantum anomalous Hall effect when tuning the time reversal symmetry by various chemical doping into the system. Using molecular beam epitaxy, we have synthesized Bi$_{2-x}$Cr$_x$Se$_3$/Bi$_2$Se$_3$–yTe$_y$ heterostructure, which was scrutinized via in situ angle resolved photoemission spectroscopy, ex situ x-ray diffraction, Raman, and x-ray photoemission characteristics analyzing techniques. We used the Hikami-Larkin-Nagaoka formula for quantifying the weak antilocalization limit in Bi$_{2-x}$Cr$_x$Se$_3$ and Bi$_2$Se$_3$–yTe$_y$ non-magnetic layer coupling near the ferromagnetic transition temperature (∼7 K). A higher concentration of Cr (1.5%) in Bi site leads to bulk carrier density for entire cooling temperature with a bandgap of 85 meV. The proximity effect of Te doped Bi$_2$Se$_3$ with magnetic topological insulator degrades the ferromagnetic response for this heterostructure. Our study suggests that the manipulation of disorder free magnetic top layer and fine tuning of spin–orbit coupling strength in the bottom topological insulator can be helpful to understand the high temperature quantum anomalous Hall effect towards relativistic quantum electronics applications.

Introduction

Magnetically coupled spin–orbit strength in non-magnetic topological insulators (MTI) pertain a major role for the rise of quantum anomalous Hall effect (QAHE) which is crucial for many potential applications [1–12]. To amend MTI, adding magnetic dopants into topological insulators (TIs) or putting TI adjacent to a magnetic layer have been adopted recently [13–19]. The latter one is called the proximity induced magnetism, which was demonstrated in Bi$_2$Se$_3$/YIG [20], Bi$_{2-x}$Cr$_x$Se$_3$/YIG [21], and Bi$_2$Se$_3$/EuS [22]. All of them have enhanced magnetism in TI layers. But on the other hand, can proximity effect also lower the magnetism of an MTI if it was put adjacent to a non-magnetic layer? To answer this question, we have prepared Bi$_{2-x}$Cr$_x$Se$_3$/Bi$_2$Se$_3$–yTe$_y$ heterostructure using molecular beam epitaxy (MBE) technique. As without the bottom layer, Bi$_{2-x}$Cr$_x$Se$_3$ shows ferromagnetic transition temperature around 30 K [23]. In in situ angle resolved photoemission spectra (ARPES), the bandgap does not exhibit a Dirac surface state (DSS) due to broken time reversal symmetry (TRS). We also studied the magnetotransport and x-ray photoemission spectroscopy (XPS) to understand the proximity effect on magnetism in the top layer by a charge transfer mechanism for the deposited heterostructure. But, beyond the limitation of atmospheric gas adsorption and bulk ferromagnetic matrix at Dirac point (DP), the protection of robust surface state and QAHE in magnetic topological insulators are considered mandatory [24–26].
Methods

All the existing layers for MTI/TI van der Waals heterostructure including a buffer layer fabrication were performed by SSI- Molecular Beam Epitaxy (MBE - Smart 100) equipped with an ultrahigh vacuum level system (base pressure \(\sim 10^{-10}\) torr). High purity Bi (99.9999\%), Se (99.999\%), Te (99.999\%), and Cr (99.999\%) were thermally evaporated through Knudsen cells. First, GaSe buffer layer was formed by annealing GaAs(111)B substrate in Se atmosphere (\(-3.4\%\) lattice mismatch in Bi\(_2\)Se\(_3\) epitaxial growth) at 480 °C for 10 min in terms of removing dangling bonds to form GaSe on As terminated GaAs(111)B surface [27]. Then, 5 quintuple layers (QLs) of Bi\(_2\)Se\(_{2\times\gamma}\), a second nonmagnetic interface layer were imprinted by the co-evaporation of Bi, Se, and Te at 525 °C, 103 °C, and 255 °C for 10 min. Eventually, the formation of thick 10 QLS of Bi\(_2\)Cr\(_\gamma\)Se\(_3\) on 5 QLS of Bi\(_2\)Se\(_{2\times\gamma}\)/GaSe were formed when Bi, Cr, Se sources were evaporated at 525 °C, 1030 °C, and 115 °C. Optimal Bi to Se flux ratio was kept at 1:10 for each layer-by-layer epitaxial growth. The growth rate of 0.5 QL/min remains almost constant for Bi\(_2\)Cr\(_\gamma\)Se\(_3\) and Bi\(_2\)Se\(_{2\times\gamma}\)/GaSe, which were determined from tuning the reflection high energy electron diffraction (RHEED) intensity oscillations. During the entire growth, the substrate temperature was maintained at 155 °C under Se rich condition to avoid the chalcogens deficiency in the deposited heterostructure film. After the growth, the film was annealed at 200 °C to eliminate the internal stress and improve the homogeneity of MTI/TI film.

The epitaxial growth optimized high quality MBE grown film were characterized by x-ray diffraction (Bruker D8 Discover single crystal diffractometer, \(\lambda = 1.5406\) Å), XPS (PHI 5000 VersaProbe, FWHM \(\leq 1.0\) eV, Al K\(_\alpha\)), and Magnetotransport analysis through six Hall probe geometry (Oxford 14 T magnet, Keithley 6221 AC/DC current source and SR830 lock-in amplifier system down to 1.6 K) experiments.

Results and discussion

Figures 1(a) and (b) show a schematic of the heterostructure and in situ RHEED real growth condition with single crystalline (1 \(\times\) 1) streaky patterns. The strong (00 l) diffraction of rhombohedral (R\(3\) \(m\)) c growth axis perpendicular to the substrate has been observed from an x-ray diffraction pattern as shown in figure 1(c). Except the three (003) and six-fold (006) periodicity peaks pertaining in-plane rotations observed upto the (0021) plane shows no additional peak, which reveals the substantial crystalline nature and epitaxial growth of
Bi$_2$−$_x$Cr$_x$Se$_3$ heterostructures. Here, the diffraction peak (0021) at 37.5° is quite profound as observed in case of Bi$_2$Se$_3$ epitaxial films [28]. The full width at half maximum (FWHM) of (003) and (006) major intensity peaks are 4.5° and 6.7° respectively. After comparison, the overlapping of Bi$_2$Se$_3$ (009) diffraction curve into the main peak of GaAs(111)B (2θ ~ 27°) was inviolably not considered for remaining analysis. From the observed (00l) diffraction peak of Bi$_2$−$_x$Cr$_x$Se$_3$, the c-axis lattice parameter was calculated to be 28.55 ± 0.02 Å for x = 0.17 concentration. Two dimensional RHEED pattern was used to estimate a-axis lattice constant from its d-spacing value (a = 3.98 ± 0.01 Å). In our case, the decreasing of both ‘a’ and ‘c’ values are due to the substitutional effect rather than the insertion of Cr between the QLs of Bi$_2$Se$_3$ can be affirmed from the d-spacing acquired from the RHEED images. This thin film heterostructure has a moderate root mean squared (RMS) roughness of 0.55 nm as observed from the AFM images (see figure 1(e)).

We further investigated the local structure from the vibrational modes of Bi$_2$−$_x$Cr$_x$Se$_3$/Bi$_2$Se$_3$−$_x$Te$_x$ heterostructure recorded using Raman spectra as shown in figure 1(d). Three active main peaks $A_{1g}$, $E_g$, and $A_{1g}$ apart from IR Raman active modes have been observed at 71 cm$^{-1}$, 130 cm$^{-1}$ and 172 cm$^{-1}$, which are close to Se rich Bi$_2$Se$_3$ QLs stretching and bending vibrational modes respectively [28, 30]. The ex situ x-ray photoemission spectra for 10 QLs Bi$_2$−$_x$Cr$_x$Se$_3$ are depicted in figures 2(a)–(c). The constituent elements of Bi$_2$−$_x$Cr$_x$Se$_3$ top layer core levels peaks are Bi (4f), Cr (2p), and Se (3d). The longer exfoliated sample exhibits other surface doping mechanism as a signature of native oxidation content (O$^{1+}$−531 eV) and hydrocarbon (C$^{13}$−284 eV) mixture from the ambient air adsorption effect (see figure 2(d)). The core level peaks of Bi (4f) is well fitted with corresponding Bi (4f) energy levels of about 162.1 eV and 156.7 eV [31]. Similarly, chromium 3$^+$ oxidations peaks can also be fitted for the 2p binding energy levels of 585.2 eV and 575.3 eV [29]. We see that the atomic concentration values of Cr ~1.5% for Bi$_2$−$_x$Cr$_x$Se$_3$ and Te ~10.5% in Bi$_2$Se$_3$−$_x$Te$_x$ at the initial peaks of Bi (4f), Cr (2p), Se (3d), Te (3d) binding energy levels. From Bi$_2$Se$_3$ core level XPS spectra, the top layered Bi (4f) and Se (3d) peaks are strongly red shifts (more than 1.3 eV) to 156.7 eV and 51.8 eV. The binding energies that correspond to 3$^{1+}$ (2p) oxidation state of bulk Cr are 584 eV and 575 eV, which is smaller than our observed Cr (2p) values. The spin–orbit coupling strength gradually varied from Bi

Figure 2. Ex-situ core level XPS spectra of annealed Bi$_2$−$_x$Cr$_x$Se$_3$ film. (a) Bi (4f), (b) Cr (2p), and (c) Se (3d) peaks. (d) XPS survey spectrum represents C (1s) and O (1s) core level peaks. Red and blue solid filled areas are obtained after Lorentzian and Gaussian line shapes fitting.
(4 f) to Cr (2p) as a consequence of the blue shift between them as well as large splitting of binding energy levels (−9 eV) rather than Cr-Se bond contribution was observed [14]. From XPS, the electron doping effect on the surface caused by a residual atmospheric gas molecule absorption plays the major role for inducing charge transfer effect [32].

Dependence of in-plane longitudinal (Rxx) and transverse resistance (Rxy) on temperature and magnetic field measurements was performed and the response is as shown in figures 3(a)–(d). Non-monotonic change of resistance till 2 K can be clearly seen in figure 3(a). Below 10 K, there have been metallic to insulator transition denoted as Tc, similar to the mechanism found in diluted magnetic semiconductors (DMS) and other relative magnetic topological insulators [33]. It is noted that the observed Tc is still lower than Bi2−xCrxSe3 [23]. A carrier dependent metallic phase with the reduction of temperature has been observed in bulk Bi2Se3 and Bi2Se3−xTex (x = 0.9) topological insulators [34, 35]. A sharp upward Rxx versus T insulating curve near Tc was observed as shown in the inset of figure 3(a). In figure 3(b), a signature of weak antilocalization (WAL) behavior in low magnetic field range at above 3 K exhibits 2D surface conducting states, which is immune to defects scattering. Further, we observe a crossover to weak antilocalization (WAL) from weak localization (WL) characteristic as seen from the upward (Λ) to downward (V) Rxy versus B curve shifts with respect to temperature. Cr doping in the place of Bi for more than x ∼ 0.10 on Bi2Se3 and Bi2Te3 at low temperature was ascribed by WL with classical parabolic dominated magneto-resistance (MR) as reported previously [33, 36]. A notable finding of WAL from the overlapping of magnetoconductance pattern is still absent even in low magnetic fields and wider cooling temperature up to 30 K from 1.6 K for Bi2−xCrxSe3/Bi2Se3−xTex heterostructure. To understand the 2D quantum correction over WAL and WL surface magnetoconductance (Δσxx) channels, we used the Hikami-Larkin-Nagaoka (HLN) relation [37]:

\[ \Delta \sigma_{\text{xx}}(B) \cong \alpha \sigma_{\text{xx}}(B) - \sigma_{\text{xx}}(0) \cong \frac{e^2}{4\pi^2} \psi\left(1 + \frac{h}{B l_0} - \ln \left(\frac{h}{B l_0}\right)\right) \]

The specific coefficients in HLN model denoted as, \( \alpha \) is the elementary charge, \( h \) is Planck’s constant, \( B \) is the applied magnetic field, \( \Psi \) is the digamma function, and the coefficient of \( \alpha \) is the representative of WAL (negative) or WL (positive) indicator from different conducting channels. The characteristic magnetic field strength \( B_0 = h/4e\alpha l_0^2 \), in which \( l_0 \) is the dephasing coherence length. Excellent fitting of HLN equation yields \( \alpha = 0.64 \) with coherence length factor \( l_0 = 107 \text{ nm} \) (figure 3(c)). This indicates that our top layered MTI has a single Dirac surface state with the moderate contribution of bulk carrier–dominated typical WL behavior at low temperature.

The anomalous Hall effect (AHE) of this semimagnetic 10 QLs Bi2−xCrxSe3/5 QLs Bi2Se3−xTex were examined from Rxy versus B plot at various temperatures and are shown in figure 3(d). Both in the positive and negative magnetic field sweeping directions, the Hall resistance yields a negative slope for several cooling temperatures which in turn is points out electron as the intrinsic majority carriers. An indistinct ferromagnetic hysteresis is clearly seen up to 7 K and thereafter hysteresis quite vanishes as depicted in figure 3(d) inset. A ferromagnetic Curie temperature (Tc) would be verified in two different ways for the identification of AHE; i) a disappearance of \( H_i \) in between below and above \( T_c \) expected region from \( R_{xy} \) isothermal hysteresis curves (see figure 3(f)), and ii) the execution of Arrot plots (R2 versus B/Rxy) in figure 3(e), in which R2 axis zero intercept towards near ferromagnetic Tc constituency [3]. From these analyses, we conclude that Tc is represented as ∼7 K for this MTI heterostructure. To understand the bulk carrier influences in AHE signal other than Dirac electron on a 2D surface, we extract the Hall coefficient of the sample using Rxy = 1/en, where e is the electron charge and n is defined as carrier concentration. We have also estimated the effective mobility using the Drude model [\( \mu(T) = R_{xy}(T)/\rho_{xy}(T) \)]. Bulk electron carrier density was found to be ∼1014 cm−2 with relatively less mobility (∼18 cm2 V−1 s−1) at lower temperatures. This is comparatively two orders higher than bulk and epilatix films of Bi2Se3 and Bi2Te3 [36]. Furthermore, higher concentration of Cr (x > 0.20) supplies more free charge carriers in the form of holes in Bi2Te3, Sb2Te3 and electrons in Bi2Se3 as a result of impregnable chemical potential disorder around the Dirac point [36, 38]. We conclude that this scenario would be a descriptive of non-localized bulk carrier scattering rather than localized Dirac surface electrons in the vicinity of \( T_c \), for this heterostructure.

Discrimination of bandgap size of 10 QLs Bi2−xCrxSe3 with a relative change of chemical potential on Fermi level by residual bulk carrier concentration can be explained using ARPES surface band structure carried out at room temperature as shown in figure 1(f). Obviously, more than 1.5% of Cr bulk doping in the place of Bi would destruct the Dirac surface state. In our case, the size of the energy gap was 85 meV, which is comparable to other Cr and V doped Bi2Se3 magnetic topological insulator for x > 0.10 concentration [31, 32]. This energy gap resides ∼130 meV from a Fermi level and the momentum broadening of the surface state is also seen by a bulk doping effect. Besides, a residual gas condensation on the topmost layer is also playing an important role in the resemblance of the bulk charge carrier effect. So, the bulk band gap size more moderately reduces rather than preserving the Dirac surface state for this magnetic topological insulator. Therefore, either controlling of bulk carrier density around DP by charge transfer coupling between the interface of MTI/TT or designing of less deficient heterostructure engineering have a significant response to the competitive realistic device applications.
Conclusion

In summary, MBE grown 10 QLs of Bi$_{2-x}$Cr$_x$Se$_3$ on Bi$_2$Se$_3-y$Te$_y$ topological insulator was extensively studied by various structural and ARPES surface band diagrammatic analyses. We found $T_c$ is lower than 10 K, which reveals that non-magnetic Te doped Bi$_2$Se$_3$ reduces the ferromagnetic order of Bi$_{2-x}$Cr$_x$Se$_3$ top layer through a proximity effect. In the ferromagnetic transition region, a weak antilocalization limit exists in the Dirac surface state coupling with non-localized bulk carrier WL interaction accompanying promptly in our magnetotransport experiments. Ex-situ XPS results indicate that an additional electron surface bonding by residual gas molecule

Figure 3. (a) A longitudinal resistance versus temperature plot. The inset shows a sharp upward insulator transition below 10 K, (b) MR curves between 1.6 K to 30 K, (c) Magnified low-temperature magnetoconductance HLN model fitting (red solid line), (d) Observation of AHE from Hall resistance at low magnetic fields and inset: field dependent $R_{xy}$ hysteresis pattern, (e) the Arrott’s plot, and (f) $H_C$($R_{AHE}$) versus T curves.
further weakens the TI surface state and anomalous Hall effect. In another term, this MTI/TI heterostructure does mimic the same TRS broken bulk insulating state as similar to a trivial insulator system.

Acknowledgments

This work is supported by the National Key Research and Development Program of China (No. 2016YFA0300803, 2017YFA0206304), the National Basic Research Program of China (No. 2014CB921101), the National Natural Science Foundation of China (No. 61674079).

ORCID iDs

Moorthi Kanagaraj  https://orcid.org/0000-0001-7339-714X

References

[1] Yu R, Zhang W, Zhang H J, Zhang S C, Dai X and Fang Z 2010 Science 329 61–4
[2] Kou X et al 2014 Phys. Rev. Lett. 113 137201
[3] Kulbachinskii V A, Kaminska A Y, Kindo K, Narumi Y, Suga K, Lostak P and Svanda P 2002 Physica B Condens. Matter. 311 292
[4] Qi X L, Hughes T L and Zhang S C 2008 Phys. Rev. B 78 195424
[5] Dyck J S, Chen W, Hajek P, Lostak P and Uher C 2002 Physica B 312 820
[6] Hor Y Set al 2010 Phys. Rev. B 81 195203
[7] Chen Y Let al 2010 Science 329 659
[8] Choi J, Choi S, Choi J, Park Y, Park H, Lee H, Woo B and Cho S 2004 Phys. Status Solidi B 241 1541
[9] Dyck J S, Svanda P, Lostak P, Horak J, Chen W and Uher C 2013 J. Appl. Phys. 94 7631
[10] Lang M, He L, Xiu F, Yu X, Tang J, Wang Y, Kou X, Jiang W, Fedorov A V and Wang K L 2012 ACS Nano 6 295
[11] Chang C Z et al 2013 Science 340 167–70
[12] Chang C Z, Zhao W, Kim D Y, Zhang H, Assaf B A, Heiman D, Zhang S C, Liu C, Chan M S H and Moosera J S 2015 Nat. Mater. 14 473–7
[13] Checkelsky J G, Yoshimine R, Tsukazaki A, Takahashi K S, Kouza Y, Falsone J, Kawasaki M and Tokura Y 2014 Nat. Phys. 10 731–6
[14] Baker A A, Figueroa A I, Kummer K, Collins-McIntyre K J, Heiman D, Zhang S C, Liu C, Chan M S H and Moodera J S 2015 Phys. Rev. B. 92 094420
[15] He Q L et al 2017 Nat. Mater. 16 94–100
[16] Menshov V N, Tugushev V V, Eremeev S V, Echenique P M and Chulkov E V 2013 Phys. Rev. B. 88 224401
[17] Liu Q, Liu C X, Xu C, Qi X L and Zhang S C 2009 Phys. Rev. Lett. 102 156003
[18] Chang C Z et al 2013 Adv. Mater. 25 1065–70
[19] Kou X et al 2013 ACS Nano 7 9205–12
[20] Lang M et al 2014 Nano Lett. 14 3459–65
[21] Liu W et al 2015 Nano Letters. 15 764–9
[22] Wie P, Katsinis F, Assaf B A, Steinberg H, Jarillo-Herrero P, Heiman D and Moodera J S 2013 Phys. Rev. Lett. 110 186807
[23] Kou X, Jiang W J, Lang M R, Xiu F X, He L, Wang Y, Yu X X, Fedorov A V, Zhang P and Wang K L 2012 J. Appl. Phys. 112 065912
[24] Fan Y et al 2014 Nat. Mater. 13 699–704
[25] Zhang Y et al 2010 Nat. Phys. 6 584–8
[26] Zhao Y et al 2013 Sci. Rep. 3 3060
[27] He L, Kou X and Wang K L 2013 Phys. Status Solidi RRL 7 50–63
[28] Haazen P P J, Laloe J B, Nummy T J, Swagten H J M, Jarillo-Herrero P, Heiman D and Moodera J S 2012 Appl. Phys. Lett. 100 082404
[29] Zhang J, Peng Z, Soni A, Zhao Y, Xiong Y, Peng B, Wang J, Dresselhaus M S and Xiong Q 2011 Nano Lett. 11 2407–14
[30] Yuan J, Zhao M, Yu Y, Lu Y, Chen C, Xu M, Li S, Loh K P and Bao Q 2015 Materials 8 5007–17
[31] Yilmaz T, Hines W, Ahraddad S, Budnica J L and Sinkovic B 2013 Phys. Chem. Chem. Phys. 15 3064–8
[32] Yilmaz T, Hines W, Sun F C, Hietkoscis I, Budnica J, Valla T and Sinkovic B 2017 Applied Surface Science 407 371–8
[33] Liu M et al 2012 Phys. Rev. Lett. 108 056805
[34] Liu R, Tan X, Ren G, Liu Y, Zhou Z, Liu C, Lin Y and Nan C 2017 Crystals 7 257
[35] Cha J A, Kong D, Hong S S, Analyst J G and Lai K 2012 and Cui Y 2011 Nano Lett. 12 1107–11
[36] Bao L, Wang W, Meyer N, Liu Y, Zhang C, Wang K, Ait P and Xia F 2013 Scientific Reports 3 2391
[37] Hikami S, Larkin A I and Nagaoka Y 1980 Prog. Theor. Phys. 63 707–10
[38] Duffy L B, Figueroa A I, Gladczuk L, Steinke N J, Kummer K, van der Laan G and Hesjedal T 2017 Phys. Rev. B 95 224422