Topological states induced by local structural modification of the polar BiTeI(0001) surface

Sebastian Fiedler¹, Sergey V Eremeev²,3,4, Vladimir A Golyashov⁵,6, Konstantin A Kohk⁶,7, Evgueni V Chulkov⁴,9,10, Hendrik Bentmann¹ and Friedrich Reinert¹

¹ Experimentelle Physik VII and Röntgen Research Center for Complex Materials (RCCM), Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
² Institute of Strength Physics and Materials Science, 634055, Tomsk, Russia
³ Tomsk State University, 634050, Tomsk, Russia
⁴ Saint Petersberg State University, 198504, Saint Petersburg, Russia
⁵ Institute of Semiconductor Physics, 630090, Novosibirsk, Russia
⁶ Ioffe Institute, 194021 Saint-Petersburg, Russia
⁷ Novosibirsk State University, 636090, Novosibirsk, Russia
⁸ Institute of Geology and Mineralogy, SB RAS, 630090, Novosibirsk, Russia
⁹ Donostia International Physics Center (DIPC), E-20018 San Sebastián/Donostia, Basque Country, Spain
¹⁰ Departamento de Física de Materiales and Centro Mixto CSIC-UPV/EHU, Facultad de Ciencias Químicas, Universidad del País Vasco/Euskal Herriko Unibertsitatea, Apdo. 1072, E-20080 San Sebastián/Donostia, Basque Country, Spain

E-mail: Hendrik.Bentmann@physik.uni-wuerzburg.de

Keywords: topological insulator, Rashba effect, spin–orbit interaction at surfaces

Supplementary material for this article is available online

Abstract
The layered polar semiconductor BiTeI exhibits large Rashba-type spin–orbit splittings in its bulk and surface electronic structure. Here we report an artificial structural modification near the surface of BiTeI(0001) induced by annealing in vacuum. Using scanning tunneling microscopy we show that the annealing-induced change in the near-surface stoichiometry results in a structural change from a non-centrosymmetric triple-layered to a quintuple-layered structure. The structural change gives rise to the emergence of topological surface states with helical spin texture as demonstrated by angle-resolved photoemission experiments and relativistic first-principles calculations. The results provide a way to modify the electronic structure of layered materials by a controlled manipulation of the atomic stacking sequences.

1. Introduction

Exploiting the spin–orbit interaction in heavy-element semiconductors for electrical spin manipulation provides perspectives for spintronic applications [1–3]. In the presence of a broken inversion symmetry spin–orbit coupling lifts the spin degeneracy of electronic states and gives rise to a momentum-dependent spin polarization, as described, e.g., by the Rashba model [4]. Such spin–orbit splittings appear in two-dimensional electron systems, e.g., at surfaces and interfaces, or even in the bulk for the case of non-centrosymmetric crystal structures. They give rise to spin-dependent transport phenomena, such as the intrinsic spin Hall effect [5] and the spin Galvanic effect [6]. On the other hand, semiconductors with a non-trivial topology in the bulk electronic structure feature topological surface states [7] with similar spin-momentum textures as for the Rashba effect. Here, strong spin–orbit coupling is crucial to induce an inverted band ordering, a key mechanism for the formation of topologically non-trivial band structures, which enable for dissipationless spin transport. In order to utilize these effects in spintronic applications it is crucial to establish ways that allow for a controlled manipulation of Rashba-split and topological states.

In the layered polar semiconductors BiTeX (X = Cl, Br, I) giant Rashba splittings in the bulk and surface band structures have been observed [8–17]. It has been shown theoretically that the size of the Rashba splitting in...
these compounds depends sensitively on details of the crystal structure, consisting of Te–Bi–I trilayers weakly coupled by van der Waals interaction, and the chemical bonding between adjacent atomic layers [18]. Furthermore, for BiTeI a topological phase and a tunable Rashba coupling have been predicted, which, however, require the application of external pressure [19]. Besides, recently it was shown that a two-dimensional topological insulator phase in BiTeI can be realized in the ultra thin films constructed from two inversely stacked trilayers [20, 21]. For BiTeCl the existence of topological surface states even at ambient pressure has been found [22, 23], in contradiction, however, to the majority of experimental results [15, 16, 24] and theory [9]. The controversy is likely related to deviations in the atomic stacking geometry and the chemical stoichiometry near the surface as well as to crystalline defects [22–24], both influencing the electronic structure of the surface and potentially its topological properties. Recently, different heterostructures involving structural units of BiTeX have been proposed to form topological states, possibly even coexisting and interacting with Rashba-split states [25, 26]. In the light of the above findings, the BiTeX semiconductors constitute a promising platform to manipulate topological and Rashba-split states via control of the local atomic geometry and the chemical composition near the surface.

In the present work we report on a structural phase change near the surface of BiTeI(0001), induced artificially by vacuum annealing. We show that an annealing-induced modification in stoichiometry and atomic stacking sequence within a near-surface region is accompanied by a structural phase change from non-centrosymmetric BiTeI to a tetradymite Bi2Te3-like structure that exhibits topological surface states. The modifications in the geometric and the electronic structure are observed by electron diffraction (LEED, RHEED), scanning tunneling microscopy (STM), angle-resolved photoemission spectroscopy (ARPES) and x-ray photoemission spectroscopy (XPS). Density functional theory (DFT) calculations suggest the possibility to obtain topological phases in the Bi2Te3-I-type structure, which is identified as the most likely candidate for the modified near-surface phase. Our results provide a pathway to induce topological states in layered semiconductors by local structural modifications.

2. Experimental and theoretical methods

BiTeI crystals were grown by mixing stoichiometric amounts of Bi2Te3 and BiI3 [27]. Samples were clamped to the sample holder and cleaved at a pressure of $10^{-10}$ mbar with a rod glued on top. The experimental setup is equipped with an Omicron VT-STM (variable temperature), a Scienta R3000 electron analyzer, a non-monochromated Al Kα x-ray gun ($hν = 1.486.6$ eV), a non-monochromated He discharge lamp ($hν = 21.2$ eV) and a SPECS ErLEED [28]. The experiments have been performed at room-temperature. The dichroic spectra were measured using circularly polarized synchrotron radiation at the UE 112 beamline of BESSY storage ring (Berlin, Germany) employing a Scienta R4000 electron analyzer. The angle of light incidence was $45^\circ$ and the plane of incidence was perpendicular to the resolved in-plane wave vector component. STM data have been processed with WSxM [29]. XPS spectra were corrected for satellites of the x-ray gun.

The RHEED analysis was performed in situ by use of built-in diffractometer at 30 kV. We have carried out an image analysis via a special software developed in [30]. The software allows one to plot 3D projections of RHEED patterns in the reciprocal space for concrete zone axis. To build 3D projections, a series of a few hundreds RHEED patterns measured at different azimuth angles with $0.2^\circ$ step was numerically combined in a 3D array of points. Using this array we may study every slice or every projection of 3D reflection map built such way.

The DFT calculations for centrosymmetric quintuple-layer (QL)-structured Bi2Te3-I phase were performed by using the VASP code [31, 32]. We used the all-electron projector augmented wave (PAW) basis sets [33, 34] with the generalized gradient approximation [35] to the exchange correlation (XC) potential. Relativistic effects, including spin–orbit coupling, were taken into account. To consider the effect of dispersion van der Waals interactions we use the DFT-D3 method by Grimme [36]. Both lattice parameters and internal atomic positions in Bi2Te3-I bulk structure were optimized. The obtained equilibrium structure have been used for construction of the slab of 6-QL thickness which was used for surface calculations.

3. Results and discussion

We start our discussion of the structural change at the BiTeI(0001) surface on the basis of STM experiments. Figure 1 (a) shows a 500 nm × 500 nm STM image of BiTeI(0001) at $–0.4$ V gap voltage and 0.1 nA tunneling current. Due to bulk stacking faults and the non-centrosymmetric unit cell, Te (bright) and I (dark) terminations coexist on the surface [28]. The steps between terraces have a height of 0.7 nm, which corresponds to the thickness of a Te–Bi–I trilayer [37]. The intensities in the LEED pattern of this surface show a sixfold symmetry at $E_0 = 50$ eV (see inset of figure 1(a)).
Figure 1. Structural changes of the BiTeI(0001) surface upon vacuum annealing. (a) Shows an STM image of a BiTeI(0001) surface with coexisting Te (bright) and I (dark) terminations, as obtained by cleaving a crystal at room-temperature. After annealing to 200 °C for 15 min the surface morphology becomes inhomogeneous, as seen in the STM image in (b). Upon further annealing at 230 °C for 15 min a structural reordering takes place. The step edge height between neighboring terraces is determined to 1 nm (inset in (d)), deviating from the value 0.7 nm found for BiTeI(0001). Please note the different length scales of the images (a)–(c). In (a)–(c), insets display LEED images of the respective surfaces ($E_0 = 50$ eV). Panel (d) shows the $dI/dV$ image corresponding to (c), simultaneously taken at the same tunneling parameters.

Figure 1(b) shows a 1 μm × 1 μm scan at −0.1 V and 0.2 nA of the same sample after annealing at 200 °C for 15 min. The surface displays a complex and inhomogeneous morphology. The LEED pattern of this surface shows broader spots with lower contrast than for the cleaved surface in figure 1(a), presumably indicating an enhanced structural disorder. Figure 1(c) shows a 1 μm × 1 μm STM image at −0.2 V and 0.2 nA after additionally heating the sample to 230 °C for 15 min. The resulting surface shows a homogeneous electronic structure. That is, in contrast to BiTeI(0001) [38], no coexistence of areas with different terminations are observed in the differential conductance map shown in figure 1(d). Note that, unlike in figure 1(a), the contrast between bright and dark areas in (c) is, therefore, a result of different heights and not of different surface terminations. Interestingly, the step heights measured for the surface in figure 1(c) are 1 nm high (see inset in (d)). This indicates that a structural change occurred at the surface. This is in line with the LEED pattern measured at $E_0 = 50$ eV that now shows a threefold symmetry in the spot intensities. Re-cleaving the same sample exposes again a BiTeI(0001) surface, like the one shown in figure 1(a). This confirms that this structural change under vacuum annealing does not affect the bulk structural properties. One possibility could be the formation of Bi$_2$Te$_3$(0001) near the surface, which has a layered tetradymite crystal structure with a structural unit (QL) height of 1 nm [38], well matching the step height measured for the annealed surface (figure 1(d), inset). However, the XPS data discussed below indicates the presence of I in the newly formed surface structure. In a LEED measurement at $E_0 = 50$ eV on a single-crystalline Bi$_2$Te$_3$(0001) surface we also found a more sixfold
observed that the work function for the surfaces shown in symmetry in the spot intensities

Figure 3 projection of BiTeI and tetradymite-like coincides with the simulation for this structure with LEED data shown in the inset of the tetradymite crystal structure of Bi2Te3 and Bi2Te2I. It is clearly seen that the distance between the spots substantially by a factor of approximately 1.6. Red circles in inter-streak distance, but the distance between the diffraction spots in the individual streaks changes from those for BiTeI (data for BiTeI before vacuum annealing. Heating the sample to 200 °C shows XPS data of the Te 4d, I 4d, and Bi 5d core level lines for the surfaces in 2018 shows a LEED-like RHEED reciprocal space map. These data are in agreement with the reciprocal space map; (c) two superimposed model diffraction spot meshes corresponding to BiTeI (blue circles) and tetradymite-like (red circles) reciprocal space cross-sections by (110) plane. Transition of (P3) space group of BiTeI into (R-3 m:H) space group is accompanied by a narrowing of the distance between the reflections lying along the [001] direction by approximately a factor of 1.6.

Figure 2. RHEED reciprocal space maps of BiTeI(0001) with superimposed model reflections (marked by circles). Main crystallographic axes are marked by arrows. The RHEED beam direction is perpendicular to the image plane. (a) Atomically flat BiTeI (0001) surface before annealing. (b) RHEED reciprocal space map of BiTeI(0001). There is no change of the surface before annealing. (c) Structural transformation into the structure with (R-3 m:H) symmetry (tetradymite-like). (d) LEED-like projection of BiTeI and tetradymite-like (R-3 m:H) reciprocal space map; (e) two superimposed model diffraction spot meshes corresponding to BiTeI (blue circles) and tetradymite-like (red circles) reciprocal space cross-sections by (110) plane. Transition of (P3) space group of BiTeI into (R-3 m:H) space group is accompanied by a narrowing of the distance between the reflections lying along the [001] direction by approximately a factor of 1.6.

symmetry in the spot intensities (not shown) than in our observations for the surface in figure 1(c). We also observed that the work function for the surfaces shown in figure 1(b) (4.5 eV) and (c) (4.3 eV) differ substantially from those for BiTeI (5.2 eV) and Bi2Te3 (5.1 eV) [24].

The results of RHEED measurements of BiTeI before (a), during (b) and after (c) annealing are shown in figure 2. Before annealing the surface of BiTeI(0001) is atomically flat, which follows from the streaks in figure 2(a). According to the changes of the RHEED patterns in (a)–(c), the structural modification upon annealing occurs in several stages. At the first stage the roughness of the surface begins to increase at 250 °C–320 °C without a change of the structure. An evidence of the roughness is the formation of 3D spots observed on the streaks in (b). Such spots are characteristic for the formation of small islands on the top of a flat surface. The blue circles in (a), (b) correspond to the modeled diffraction pattern according to the BiTeI crystal structure.

At the second stage the RHEED pattern changes in the [1 1 0] direction (figure 2(c)). There is no change of the inter-streak distance, but the distance between the diffraction spots in the individual streaks changes substantially by a factor of approximately 1.6. Red circles in (c) demonstrate the result of a simulation based on the tetradymite crystal structure of Bi2Te3 and Bi2Te2I. It is clearly seen that the distance between the spots coincides with the simulation for this structure with (R-3 m:H) space group. Figure 2(d) shows a LEED-like projection of BiTeI and tetradymite-like (R-3 m:H) reciprocal space map. These data are in agreement with the LEED data shown in the inset of figure 1. Figure 2(e) shows the two superimposed model diffraction spot meshes from (b) and (c), corresponding to the BiTeI (blue circles) and tetradymite-like (red circles) reciprocal space cross-sections along the (1 1 0) plane.

To further characterize the observed structural change we performed XPS and ARPES measurements. Figure 3(a) shows XPS data of the Te 4d, I 4d, and Bi 5d core level lines for the surfaces in figures 1(a)–(c). The measurements were done under an emission angle of 60° to enhance the surface sensitivity. The black line shows data for BiTeI before vacuum annealing. Heating the sample to 200 °C (blue line) and subsequently to 230 °C (red) results in a decreased relative intensity of the I 4d core level by ca. 40%, when normalized to the Bi 5d
intensity. The intensity ratio between Te and Bi shows a slight increase only. We further note a small energy shift by ca. 0.1 eV of the Te 4d and Bi 5d core levels towards lower binding energies. Overall the data indicate a slight energy shift \( \gamma \) and \( \alpha \) band splitting. Figure 3

Another consequence of the annealing, seen \( \beta \) and \( \gamma \) is a pronounced change of the overall valence band structure up to binding energies of \( \approx 3 \) eV. In particular, in figure 3(d) we find an electron-like band \( \beta \) at approximately 1.25 eV binding energy and a hole-like band \( \gamma \) at approximately 1.8 eV. Similar states were found in ARPES experiments and DFT calculations for Bi\(_{2}\)Te\(_{3}\)(0001)\(^{39}\) and were identified as surface states, being mainly derived from p\(_{x}\) orbitals of the surface-terminating Te layer. We therefore anticipate that the features \( \beta \) and \( \gamma \) are surface bands. The similarity of these bands to the case of the Bi\(_{2}\)Te\(_{3}\)(0001) surface is in line with the suggested formation of Bi\(_{2}\)Te\(_{3}\)I(0001), whose surface is expected to be terminated by a Te layer and a Bi layer below. We note that these surface states are also observed for a sputtered-annealed sample at the same binding
energies and with the same dispersions, whereas the near-$E_F$ electronic structure deviates between annealed and sputtered-annealed samples (see supplemental material, figure S4).

We will now consider the band $\alpha$ in more detail. The second-derivative of figure 3(d) is presented in figure 4(a). The data indicate a gapless Dirac-like dispersion with the Dirac point at $\approx 0.4$ eV. This deviates from both the Rashba-type band structure of the non-centrosymmetric BiTeI phase and also from the band structure of a cleaved Bi$_2$Te$_3$(0001) single crystal (see supplemental materials, figure S3). The hallmark feature of a topological Dirac state is the opposite spin orientation for opposite sign of momentum and its inversion passing through the Dirac point. In order to address the spin polarization of the band $\alpha$ we have performed dichroic ARPES measurements using circularly polarized light, as shown in figure 4(b). The dichroic data were taken in the direction perpendicular to the plane of light incidence.

As is evident from the data in figure 4(b) the band $\alpha$ shows a pronounced circular dichroism, which switches sign (red/blue) for opposite momentum directions (negative/positive) in the upper part of the Dirac cone. More faintly at approximately 0.55 eV binding energy, we find the reversed behavior for the lower part of the Dirac cone, i.e. along negative/positive wave vectors we observe a blue/red dichroism. Such an overall sign change in dichroism between the upper and the lower Dirac cone can be associated with the spin–orbit splitting of these two branches [40], as opposed to a mere geometric effect. In general, a pronounced circular dichroism is a typical effect in photoemission from topological surface states [41]. Whereas effects of the photoelectron final state are important for a quantitative understanding of the circular dichroism [40, 42], photoemission theory indicates at least a qualitative relation to the spin polarization of the surface state [43].

This dichroic ARPES results are in a good agreement with our calculated spin-resolved electronic band structure of a Bi$_2$Te$_3$I(0001) surface, which is also plotted in figure 4(b). Note that just below the Dirac point the intensity is rather weak due to the overlap with bulk valence band states, as indicated by a comparison with the calculated bands. Furthermore, we find that the surface states $\beta$ and $\gamma$ are reproduced well in our calculation, too (see Supplemental Materials, figure S4).

It is obvious that the process of the annealing-driven structural change in the near-surface region is very complex (the kinetics of the process also depend on the pre-treatment like Ar-ion sputtering) and therefore it cannot be simulated in detail by means of DFT total energy calculations. Nevertheless, to check the plausibility of possible steps in the structural modification, we considered an I-evaporation-induced structural change one an I-terminated surface. First, we removed the iodine layer from the surface of the slab which thus became Bi-terminated. Then we swapped the first Bi- and second Te layer. This swapping can be considered as the simplest surface phase transformation since it leads to the formation of a surface Bi$_2$Te$_3$I QL: ... Te–Bi–I–Te–Bi–I–Te–Bi ... Te–Bi–I–Te–Bi–I–Bi–Te. Comparing the total energies of the relaxed initial and final structures we found

![Fig. 4](image-url)
that such a swapping provides an energy gain of 280 meV. Hence, one may speculate that the annealing-induced change of stoichiometry could be a driving force for the structural change, although, of course, the actual process is certainly much more complex than in this simplified example. Furthermore, the structural change involves the atomic layers to a depth of several nanometers, at least 5–6 nm, in order to ensure the emergence of the topological Dirac surface state.

4. Conclusion

In summary, we have shown that a local structural phase change can be induced on the (0001)-surface of the strongly spin–orbit coupled semiconductor BiTeI by annealing in vacuum. The change of the geometric structure considerably alters the electronic band structure and modifies its topology. In particular, this gives rise to the presence of topological surface states with helical spin texture. This observation indicates the opportunity to modify the topological properties and Rashba-type spin splittings in the electronic structure of layered materials by control over the atomic stacking sequences. The resulting modifications in the spin–orbit coupled band structure might be relevant for applications of two-dimensional materials for spin-based transport effects. Our findings might also facilitate the investigation of hybridization effects between spin-polarized states, arising from a non-trivial topology and from Rashba-type spin–orbit interaction, for which unconventional spin-dependent excitation phenomena have been predicted [25, 26].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft through SFB1170 (project A01), and partly by the Tomsk State University competitiveness improvement programme (project No. 8.1.01.2017), by the Russian Science Foundation (Grants No. 17-12-01047, in part of crystal growth and ARPES measurements (figure 4) and 18-12-00169, in part of DFT calculations), Russian Foundation for Basic Research (Grant No. 17-02-00729) and Saint Petersburg State University (project 15.61.202, 2015).

References

[1] Datta S et al 1990 Appl. Phys. Lett. 56 56
[2] Züricl I et al 2004 Rev. Mod. Phys. 76 523
[3] Yamada S 2005 Sci. Technol. Adv. Mater. 6 406–10
[4] Rashba E I 1960 Sov. Phys. Solid State 2 1199–22
[5] Sinova J et al 2004 Phys. Rev. Lett. 92 126603
[6] Ganichev S D et al 2002 Nature 417 153–6
[7] Hasan M et al 2010 Rev. Mod. Phys. 82 3045
[8] Ishizaka K et al 2011 Nat. Mater. 10 521–6
[9] Eremeev SV et al 2012 Phys. Rev. Lett. 108 246802
[10] Crepaldi A et al 2012 Phys. Rev. Lett. 109 096803
[11] Landolt G et al 2012 Phys. Rev. Lett. 109 116403
[12] Eremeev SV et al 2012 JETP Lett. 96 437–44
[13] Skylnadnva I Y et al 2012 Phys. Rev. B 86 094302
[14] Eremeev SV et al 2013 New J. Phys. 15 075015
[15] Landolt G et al 2013 New J. Phys. 15 085022
[16] Sakano M et al 2013 Phys. Rev. Lett. 110 107204
[17] Maaß H et al 2016 Nat. Commun. 7 11621
[18] Bahramy M S et al 2011 Phys. Rev. B 84 041202(R)
[19] Bahramy M S et al 2011 Nat. Commun. 3 679
[20] Nechaev I A et al 2017 Sci. Rep. 7 43666
[21] Eremeev SV et al 2017 Phys. Rev. B 96 155309
[22] Chen Y L et al 2013 Nat. Phys. 9 704–8
[23] Yan Y et al 2015 J. Phys.: Condens. Matter 27 475004
[24] Fiedler S et al 2015 Phys. Rev. B 92 235430
[25] Zhou J et al 2014 Sci. Rep. 4 3841
[26] Eremeev SV et al 2015 Sci. Rep. 5 12819
[27] Tomokiyo A et al 1977 Jpn. J. Appl. Phys. 16 291
[28] Fiedler S et al 2014 New J. Phys. 16 075013
[29] Horcas I et al 2007 Rev. Sci. Instrum. 78 013705
[30] Suturin S M et al 2016 J. Appl. Phys. 49 1532
[31] Kresse G et al 1993 Phys. Rev. B 48 13115
[32] Kresse G et al 1996 Comput. Mater. Sci. 6 15–50
[33] Blöchl P E 1994 Phys. Rev. B 50 17953
[34] Kresse G et al 1999 Phys. Rev. B 59 1758
[35] Perdew J P et al 1996 Phys. Rev. Lett. 77 3865
[36] Grimme S et al 2010 J. Chem. Phys. 132 154104
[37] Shevelkov A V et al 1995 J. Solid State Chem. 114 379–84
[38] Petasch U et al 1999 Z. Naturforsch. B 54 234–8
[39] Herdt A et al 2013 Phys. Rev. B 87 035127
[40] Bentmann H et al 2017 Phys. Rev. Lett. 119 106401
[41] Wang Y H et al 2011 Phys. Rev. Lett 107 207602
[42] Scholz M R et al 2013 Phys. Rev. Lett. 110 216801
[43] Mirhosseini H et al 2012 Phys. Rev. Lett. 109 036803