Direct Atom-by-Atom Chemical Identification of Nanostructures and Defects of Topological Insulators

Ying Jiang,† Yong Wang,*,‡ Jared Sagendorf,† Damien West,† Xufeng Kou,§ Xiao Wei,† Liang He,§ Kang L. Wang,§ Shengbai Zhang,*,† and Ze Zhang*,‡

†Center of Electron Microscopy and State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China
‡Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180, United States
§Department of Electrical Engineering, University of California, Los Angeles, California 90095, United States

§ Supporting Information

ABSTRACT: We present a direct atom-by-atom chemical identification of the nanostructures and defects of topological insulators (TIs) with a state-of-the-art atomic mapping technology. Combining this technique and density function theory calculations, we identify and explain the layer chemistry evolution of Bi$_x$Te$_{3-x}$Se$_x$ ternary TIs. We also reveal a long neglected but crucially important extended defect found to be universally present in Bi$_x$Te$_x$ films, the seven-layer Bi$_x$Te$_x$ nanolamella acceptors. Intriguingly, this defect is found to locally pull down the conduction band, leading to local n-type conductivity, despite being an acceptor which pins the Fermi energy near the valence band maximum. This nanolamella may explain inconsistencies in measured conduction type as well as open up a new route to manipulate bulk carrier concentration. Our work may pave the way to more thoroughly understand and tailor the nature of the bulk, as well as secure controllable bulk states for future applications in quantum computing and dissipationless devices.

KEYWORDS: Bi-based chalcogenides, topological insulators, Bi$_x$Te$_{3-x}$Se$_x$, seven-layer nanolamellae

Bi$_x$-based chalcogenides provide a fertile field for modern research and applications.1−5 In the past decades, they have been extensively investigated in the context of thermoelectric applications, due to their high thermoelectric figure of merit. After the recent theoretical prediction6 and experimental verification7 of topological insulators (TIs), such chalcogenides have experienced a resurgence of interest as holding great promise in both the search for exotic physical phenomena8−10 and the applications of future devices.11−16 However, such promise has been hampered by the residual bulk carriers, since a high bulk conductivity will overwhelm the surface states and be a detriment to the observation of the exotic properties of TIs. Although ideal Bi$_x$-based TIs have gaps in the bulk, most chalcogenides that have been synthesized to date possess metallic bulk states that result from the presence of crystal defects.17,18 Therefore, it is of the utmost importance to advance the understanding of the nanostructures, defects, and chemistries to allow for the manipulation of the bulk conductivity.

The overwhelming majority of reported work in this area has focused on the exotic properties of the surface states and transport properties of TIs by angle-resolved photoemission spectroscopy (ARPES),7 scanning tunneling microscopy (STM),19 and other electrical measurements.5 By contrast, a limited effort has been directed toward obtaining an accurate picture of the nanostructures, defects, and chemistries of TIs at atomic resolution, although such information is of critical importance to understand their demonstrated properties. To the best of our knowledge, no direct chemical imaging of the compositions of TIs at the atomic level has thus far been presented.

In this work, we use an advanced Cs-corrected scanning transmission electron microscope (STEM) attached with an energy dispersive X-ray (EDX) spectrocope and a delicate process for the STEM specimen preparation. A combination of these techniques ensures maximum X-ray collection when we map elemental distributions at a particular crystallographic zone axis, which is crucial for atomic imaging of Bi-based TI composition (details in the Supporting Information). We directly identify the layer-chemistry evolution of Bi$_x$Te$_{3-x}$Se$_x$ ternary TIs at the atomic level. We also reveal long neglected but important defects in Bi$_x$Te$_3$ films, the seven-layer nanolamella acceptors, which have been overlooked within the TI community. Our results visually demonstrate that the seven-layer nanolamella is composed of alternately stacked Bi and Te layers with the order of Te−Bi−Te−Bi−Te−Bi−Te. Both the layer-chemistry evolution of Bi$_x$Te$_{3-x}$Se$_x$ and the conduction behavior of the seven-layer nanolamellae are...
elucidated using explicit first-principles density functional theory calculations.

Bi$_2$Te$_3$ thin films were grown on intrinsic GaAs (111) substrate by molecular beam epitaxy (MBE). GaAs substrates were cleaned in acetone by ultrasonication for 15 min and then loaded into the MBE chamber. Pregrowth annealing under a Se-rich condition was performed at $\sim 580^\circ$C for 30 min to remove the native oxides from the surface of GaAs substrates. High-quality stoichiometric Bi$_2$Te$_3$ thin films were grown at 200 $^\circ$C under a Te-rich condition to achieve low defect density. High-quality single crystals of Bi$_2$Te$_2$Se and Bi$_2$TeSe$_2$ were prepared by melting stoichiometric mixtures of 99.99% pure Bi, Te, and Se. After holding at 1273 K for 24 h in silica tubes sealed under vacuum and cooling to 823 K with a cooling rate of 10 K/h, the samples were air-quenched.

Cross-sectional samples for STEM were prepared using a dual beam microscope (FIB, Quanta 3D, FEG, FEI) with gallium ion milling and precision ion polishing system (PIPS, Gatan 691) with argon ion milling. Prior to milling with FIB, an electron backscattering diffraction (EBSD) system was utilized to determine the specific crystallographic orientation ($\langle 100 \rangle$) of the film (shown in Supporting Information). Notably, further accurate investigations in STEM require confirmation of crystallographic orientation ($\langle 100 \rangle$), since only in this specific direction can the layered structure and atomic columns for individual elements (i.e., Bi and Te) be achieved. A slight deviation from $\langle 100 \rangle$ ensures a small angular tilt in STEM and thus high X-ray collection efficiency for elemental mapping. The atomic structures and defects were examined using an FEI TITAN Cs-corrected ChemiSTEM, operating at 200 kV. This instrument incorporates the functions of spherical aberration corrector and ChemiSTEM technology. A probe-corrector aids in achieving a resolution up to 0.08 nm for the HAADF-STEM image. ChemiSTEM EDX technology with a delicate STEM specimen preparation technique delivers outstanding analytical speed and sensitivity for the determination of the chemical compositions with atomic resolution.

Bi$_2$Te$_3$ is a narrow-gap layered semiconductor with tetradymite structure (space group $R\bar{3}m$) consisting of three quintuple layers (QLs) arranged along the z-axis in a unit cell. Figure 1a shows a typical high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image, projected along the crystallographic direction of Bi$_2$Te$_3$ ($\langle 100 \rangle$). Unlike that of conventional high-resolution TEM (HRTEM) images, the contrast of HAADF-STEM images is roughly proportional to $Z^2$, where $Z$ is the atomic number. Thus the atom columns with high intensity in Figure 1a correspond to Bi atoms due to a larger atomic number ($Z = 83$) and Te atoms with a smaller atomic number ($Z = 52$) appear darker in the image. The quintuple layer is clearly observed, composed of five atomic layers with a stacking sequence of Te(1)–Bi–Te(2)–Bi–Te(1). Te atoms exist in two nonequivalent atomic sites (denoted as Te(1) and Te(2)), where Te(1) layers in adjacent QLSs are held together by van der Waals interactions with a relatively large gap, while Te(2) atoms are at the center of the QL and connect tightly with Bi atoms by covalent bonds. The consistency of the layered structure in Figure 1a with Bi$_2$Te$_3$ model (Figure 1f) indicates the single crystalline nature of a high-quality film.
Further chemical identification of atom sites was performed with EDX elemental mapping with atomic resolution. The area for EDX mapping (Figure 1b) corresponds to the rectangular region in Figure 1a, including two QLs. As illustrated in Figure 1c and d, there are four Bi layers and six Te layers in the two QLs. Figure 1e represents a combination of Figure 1c and d and shows the EDX map of the Bi and Te mixture. In this image, the two kinds of atoms are marked by different colors, with red points representing Bi atoms and green points representing Te atoms. The EDX mapping results are in good agreement with the ideal structure model of Bi$_2$Te$_3$ (Figure 1f), thereby indicating the reliability of the new method.

Compared with the HAADF images, EDX maps may have a larger delocalization effect, resulting in that the van der Waals gap in Figure 1b is more clearly observed than that in Figure 1e. However, the atom position can still be confidently defined, with the center of signal area corresponding to the center of atom. Furthermore, EDX mapping technology with atomic resolution can provide the chemical information of individual atoms, especially for those materials consisting of two atoms adjacent in the periodic table or more than two atomic species, such as Sb$_2$Te$_3$ (refer to Supporting Information Figure S3) and ternary compounds Bi$_x$Te$_{3−x}$Se$_x$. Bi$_x$Te$_{3−x}$Se$_x$ ($x = 1, 2$) have recently been found to be even more promising TIs than Bi$_2$Te$_3$ (Bi$_2$Se$_3$); however, their layer chemistries have yet to be conclusively determined. From the EDX maps (Figure 2a and b, with the details presented in Supporting Information, Figures S4 and S5), we visually demonstrate that the central substitution rule only applies to the condition in Bi$_2$Te$_2$Se (Se substitutes the central-layer Te), but not to that in Bi$_2$TeSe$_2$ (explained later). Figure 2c shows the layer-chemistry evolution from Bi$_2$Te$_3$ to Bi$_2$Se$_3$ via Bi$_2$Te$_2$Se and Bi$_2$TeSe$_2$. This evolution is easily understood by considering that the formation and cohesive energy of Bi$_2$Se$_3$ is larger than that of Bi$_2$Te$_3$, indicating that the Bi–Se bond is stronger than the Bi–Te bond. If we introduce Se into Bi$_2$Te$_2$Se to form Bi$_2$Te$_2$Se, Se can substitute either the central atom Te(2) (forming six Bi–Se bonds) or one on the surface of the QL Te(1) (forming three Bi–Se bonds). Due to the large Bi–Se bond strength, Se prefers to substitute the central atom, forming Te–Bi–Se–Bi–Te. Similarly, if more Se is added to form Bi$_2$TeSe$_2$, the stability of the (Te/Se)–Bi–Se–Bi–(Te/Se) improves because such a layer-chemistry nanostructure contains nine Bi–Se bonds; by contrast, Se–Bi–Te–Bi–Se contains only six Bi–Se bonds. The results of the density functional theory calculation of the stability of Se and Te substitutional point defects are consistent with this understanding. We find that the formation energy of Se-on-Te(2) in Bi$_2$Te$_3$ is 100 meV more stable than that in Se-on-Te(1), whereas Te-on-Se(1) in Bi$_2$Se$_3$ is 250 meV more stable than Te-on-Se(2). Calculation details are presented in the Supporting Information.

In addition to the structural and chemical analysis of the ternary TIs, with this combined technique, we are also able to identify and establish the role of defect nanostructures. From previous calculations$^{24−26}$ of defect formation energies, $E_{\text{set}}$ Te$_{\text{Bi}}$ and Te$_{\text{Te}}$ are inferred to constitute the primary defects in Bi$_2$Se$_3$ and Bi$_2$Te$_3$. Despite verification of defects by STM results,$^{18,26}$ (1) STM has difficulty in accurately establishing atom sites and defect localizations, and (2) STM can only give a view to the defects present in the layers near the surface, which may be substantially different from the scenario of defects within the bulk. Consequently, defects which are restricted to the bulk region can be overlooked, despite the important role they may play in determining the carrier type and the transport properties of the examined materials. In the present work, we reveal such a neglected but important defect, the seven-layer nanolamella, in the bulk of Bi$_2$Te$_3$ films.

Deviating from the normal five-layer structure of ideal Bi$_2$Te$_3$, seven-layer lamellae have been suggested in synthesized Bi$_2$Te$_{3x}$-based thermoelectric materials (fabricated by Bridgman method) in previous studies, involving electron diffraction pattern analysis, Hall measurement, and model calculations. Controversies on the core of the seven-layer lamellae, including chemical composition and stacking sequence, prevail$^{22,27,28,31,32}$ despite the agreement among researchers on the existence of seven-layer lamellae. Interestingly, no such issue arises in the field of TIs, although such information is of significant importance to determine the carrier type and properties of topological insulators. Employing the combined technique, the distribution and combination of the elemental maps are presented in Figure 3c–e, with white dashed lines indicating the corresponding layers. Figure 3f exhibits a septet with alternating sequences of Te and Bi layers in a seven-layer lamella. The chemical composition and structure of such a seven-layer lamella is demonstrated visually as Bi$_2$Te$_4$ with an atomic arrangement of Te–Bi–Te–Bi–Te–Bi–Te, as schematically shown in Figure 3f. Intriguingly, the seven-layer lamellae cannot remain unbroken through the film but always suffer from a split, accompanied by Bi–Te atom conversion, as discussed in the Supporting Information, Figure S6.

First-principles density functional theory calculations within the local density approximation$^{36}$ were performed to determine the energetics and the electronic behavior of this seven-layer
lamella. Calculation supports the easy formation of the seven-layer lamella, yielding formation energies of only 0.015 and 0.168 eV per Bi−Te unit for the insertion of a Bi−Te bilayer to create the seven-layer lamella, under Bi-rich and Te-rich conditions, respectively. Surprisingly, the value can be lower than the energy of a stacking fault or even the (0001) surface

Figure 3. Structural and chemical identifications of the seven-layer lamellae in Bi₂Te₃. (a) HAADF-STEM image of Bi₂Te₃ projected along ⟨100⟩, showing a seven-layer lamella. (b) HAADF-STEM image of the seven-layer lamella zooming into the field marked in a. (c−d) EDX mapping results of Bi and Te, respectively. (e) EDX mapping results of the mixture of Bi and Te, demonstrating that the seven-layer lamella is Bi₁Te₄. Red points correspond to Bi atoms and green points to Te atoms. (f) Structure of seven-layer lamella in Bi₂Te₃.

Figure 4. Behavior of the seven-layer lamellae calculated by density functional theory. (a) Band structure of the neutral supercell containing the seven-layer lamellae. The open red circles, solid blue triangles, and solid black circles indicate states which have a significant real space projection in the seven-layer slab, the quintuple slab adjacent to the seven-layer slab, and the quintuple slab furthest from the seven-layer slab (most bulk-like region), respectively. The shaded region is the gap indicated by excluding bands which primarily project into the near defect region. The Fermi energy of the cell is indicated by the horizontal line at zero and is found to be below the bulk VBM. (b) Supercell used for the calculation of the band structure and energy of the Bi₁Te₄ seven-layer defect in Bi₂Te₃. (c) The ẑ-plane average of the electron potential as a function of ẑ, the positions correspond to the supercell is shown in b. The plane average is further averaged for each ẑ value over a window the thickness of a QL in the ẑ-direction. (d) Schematic of the band bending which exists in the vicinity of the seven-layer Bi₁Te₄ defect. It illustrates how the local drop in potential causes the CB to locally drop below the bulk VBM, thereby both closing the gap and leading to acceptor behavior.
energy. The valence of the additional bilayers Bi (3+) and Te (2−) leads to the assumption that the seven-layer structure would be most stable if it donated an electron to become 1+; however, such an assumption is not verified by direct calculation of the band structure of the defect cell. The presence of the defect closes the gap in the band structure, as shown in Figure 4a. Performing a real space projection of the bands onto the near-defect region (seven-layer and adjacent quintuple layer slabs) allows identification of the bulk gap in the defect supercell because the gap that exists when the states with a substantial projection in the near-defect region is excluded from the band structure. By this method, we find that the Fermi energy (E_F) of the defect supercell (indicated by the zero line in Figure 4a) falls below the bulk valence band maximum (VBM). This result agrees with the alignment between the defect band structure and the bulk band structure via the average potential in the bulk region, where the E_F of the defect cell is also found to lie below the VBM of bulk Bi2Te3.

Both results indicate that the seven-layer structure acts as an acceptor.

Insight into the nature of the accepting states can be obtained by examining the average potential in the supercell containing the lamella. Figure 4c shows that the average potential sharply declines in the vicinity of the seven-layer slab because the slab is locally electron-rich and thus a fraction of the electrons are thus spared over to adjacent QL regions. Figure 4c presents a schematic of the resulting dipoles symmetrically pointing outward from the center at z = 45 Å, leading to the downward bending of the electron potential as schematically shown in Figure 4d. Such bending causes the conducton band minimum to decrease locally below the bulk VBM.

As mentioned above, the Bi2Te3 bulk conductivity was previously attributed to point defects, such as TeBi and BiTe; however, the newly proposed defect Bi4Te5 also significantly influences both the bulk carrier concentration and conduction type. Formation energies indicate that, as Bi2Te3 is prepared under the Bi-rich growth condition, Bi4Te5 formation becomes more likely and may even dominate the electronic behavior of Bi2Te3. Nominally, the presence of the seven-layer defect is expected to open up a new route to manipulate the bulk carrier concentration without any additional elements. However, the effectiveness of the seven-layer defects in accepting electrons remains undetermined, given that the metallic gap may erase band bending and thus increase the E_F. If such an increase occurs, the formation of the seven-layer structure may effectively terminate the conversion from n- to p-type, as suggested by the experiments, where regardless of the growth condition by MBE, Bi2Te3 is always n-type. The seven-layer nanolamellae may also lead to a directionally dependent carrier type because of in-plane conductivity as well as inaccuracy in the experimental determination of the Fermi level position in transport measurements. This scenario contributes to difficulties in controlling the Fermi level in this material.

The universal existence of the seven-layer nanolamella acceptors in Bi2Te3 films grown by MBE has been verified by checking more than 10 Bi2Te3 films. Additionally, the Bi4Te5 nanolamellae are also present in the Bi2Te3 crystals as thermoelectric materials (prepared by the Bridgman method), according to earlier reports.28–30 Such a structure also exists in Sb doped Bi2Te3 (not shown here), which has been extensively investigated for their superior properties in the TI field although their atomic structure still remains unclear. Consequently, performing calculations with the seven-layer nanolamellae considered is essential to arrive at a complete understanding of the true properties of Bi-based TIs.

In summary, EDX mapping with atomic resolution can efficiently achieve a direct atom-by-atom chemical identification of nanostructures and defects in Bi-based TIs. We did not only directly identify and explain the layer-chemistry evolution of the Bi2Te3−xSex ternary TIs, but also revealed the universal existence of seven-layer nanolamella acceptors, a long neglected but important defect in Bi2Te3 films. The nature of the seven-layer nanolamella can explain inconsistencies in measured conduction type and open up a new route to manipulate the bulk carrier concentration. This work offers a pathway for revealing and elucidating new nanostructures and defects in topological insulators and may pave the way to better tailor the bulk nature of topological insulators for their future applications in dissipationless devices.

# ASSOCIATED CONTENT

* Supporting Information

Methods: Orientation identification by electron backscattering diffraction (EBSD); details about the density functional theory calculations. Figure S1: Schematic of a unit cell of Bi4Te5 projected along ⟨100⟩. Figure S2: Orientation identification by EBSD. Figure S3: Structural and chemical identifications of Sb2Te3. Figure S4: Chemical identifications of Bi2Te5Se. Figure S5: Chemical identifications of Bi2Te4Se. Figure S6: Structural and chemical identifications of the seven-lamellae in Bi2Te3. This material is available free of charge via the Internet at http://pubs.acs.org.

# AUTHOR INFORMATION

Corresponding Author
E-mail: yongwang@zju.edu.cn (Y.W.), zhangs9@rpi.edu (S.B.Z.), and zezhang@zju.edu.cn (Z.Z.).

Author Contributions
Y.W. conceived the research for atomic imaging of the structure of topological insulators. Y.J. and Y.W. conducted the STEM/EDX experiments with assistance from X.W., X.F.K., L.H., and Z.Z. K.L.W grew the MBE samples. J.S., D.W., and S.B.Z. carried out the calculations. All participated in the analysis and discussion.

Notes
The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

We acknowledge the support of National Science Foundation of China (No. 11174244), the National 973 Program of China (2013CB934600, 2009CB623700), Zhejiang Provincial Natural Science Foundation of China (LR12A04002), National Young 1000 Talents Program of China and the Fundamental Research Funds for the Central Universities. J.S. acknowledges the support of NSF award DMR 0850934 and Department of Energy (DOE) Grant No. DE-SC0002623. D.W. and S.B.Z. acknowledge the support of Defense Advanced Research Project Agency (DARPA) Award No. N66001-12-1-4034. K.W. acknowledges the support of the Focus Center Research Program-Center on Functional Engineered Nano Architectonics (FENA) and DARPA. Y.W. acknowledges Prof. Jinfeng Jia at Shanghai Jiaotong University for providing bulk Bi2Te2Se and Bi2Te3 samples.
REFERENCES

(16) Kong, D. S.; Cui, Y. Nat. Chem. 2011, 3 (11), 845–849.