Termination dependent topological surface states of the natural superlattice phase Bi$_4$Se$_3$

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Abstract

We describe the topological surface states of Bi$_4$Se$_3$, a compound in the infinitely adaptive Bi$_2$-Bi$_2$Se$_3$ natural superlattice phase series, determined by a combination of experimental and theoretical methods. Two observable cleavage surfaces, terminating at Bi or Se, are characterized by angle resolved photoelectron spectroscopy and scanning tunneling microscopy, and modeled by ab-initio density functional theory calculations. Topological surface states are observed on both surfaces, but with markedly different dispersions and Kramers point energies. Bi$_4$Se$_3$ therefore represents the only known compound with different topological states on differently terminated surfaces.
Three-dimensional topological insulators (3D TIs) are a new class of materials that exhibit topologically protected spin-chiral metallic topological surface states (TSS) and a bulk band gap [1-12]. The great interest in 3D TIs is partly due to the fact that they necessarily host exotic bound states at their boundaries when interfaced with other non-topological or topological materials [13]. In addition, several theoretical studies have predicted that novel properties may emerge when topological insulators are interlaced with other materials in a regular superlattice [14, 15]. One expectation is that by combining topological and trivial layers into a superlattice, it might be possible to dramatically enhance the transport contribution of topological states from the interfaces. Another interesting possibility would be to stack the layers of 2D TIs in a weakly interacting superlattice and turn the edge states of individual layers into a topological surface state of a “weak” TI crystal. In order to pursue these promising avenues, however, various experimental challenges have to be solved. For example, a basic understanding of the surface band structures of more complex topological materials, while highly desirable, is not trivial. Although there have been studies of different materials at the interface of 3D TIs [16, 17], no in depth study of the TSS and electronic band structure of a complex topological material, or a true bulk topological superlattice material has yet been reported.

Here we investigate the properties of Bi$_4$Se$_3$, the simplest topological superlattice material, consisting of single Bi$_2$ layers interleaved with single Bi$_2$Se$_3$ layers in a 1:1 ratio. It is therefore a natural superlattice of two intensely studied topological materials. While bulk Bi$_2$Se$_3$ is a model 3D TI, an isolated Bi$_2$ layer is predicted to be a 2D TI [18] and combining these two building blocks into a 3D superlattice offers a unique possibility for studying the effects of inter-layer interactions. We investigate the electronic structure of this material experimentally via angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM) and theoretically via ab-initio density functional theory (DFT) calculations. We observe two types of surfaces after cleaving the crystal, corresponding to Bi$_2$ and Bi$_2$Se$_3$ terminated terraces. We find that both terminations exhibit TSS, but with substantially different Kramers point energies and dispersions. We show that many features of the surface band structure can be derived from the idealized case of weakly coupled Bi$_2$ and Bi$_2$Se$_3$ layers where the interaction between these building blocks is responsible for the different TSSs. This suggests that Bi$_4$Se$_3$ and related Bi$_2$\(m\)Bi$_2$Se$_3$\(n\) [19] superlattice phases provide a unique opportunity for studying the coexistence of multiple types of
topological surface states on different cleavage surfaces in the same material.

Crystals of Bi$_4$Se$_3$ were grown by slow cooling a Bi-rich melt. The crystal structure and quality were confirmed by X-ray diffraction. The ARPES experiments were carried out on a Scienta SES-100 electron spectrometer at beamline 12.0.1 of the Advanced Light Source. The spectra were recorded at photon energies ranging from 35 to 100 eV, with a combined instrumental energy resolution of $\sim$15 meV and an angular resolution better than $\pm 0.07^\circ$. The combined spatial resolution, dependent upon precise linear motion control of the sample and the 60 $\mu m$ photoemission spot size of the beam, was better than 80 $\mu m$. Samples were cleaved at 15-20 K under ultra-high vacuum (UHV) conditions. The temperature was measured using a silicon sensor mounted near the sample. Photoemission Electron Microscopy (PEEM) experiments were carried out at the XPEEM/LEEM end-station at the National Synchrotron Light Source beamline U5UA at room temperature with 47.8 eV photons using an Elmitec SPELEEM III microscope. All the samples were cut from the same bulk piece and cleaved and measured in ultrahigh vacuum conditions (base pressure better than 2 x 10$^{-9}$ Pa in the ARPES chamber and better than 2 x 10$^{-8}$ Pa in the PEEM chamber). Samples for STM measurements were cleaved in-situ under ultra-high vacuum conditions, with the measurements performed at 4.2 K.

Surface electronic structure calculations were performed in the framework of density functional theory using the Wien2k code [20] with a full-potential linearized augmented plane-wave and local orbitals basis together with the Perdew-Burke-Ernzerhof parameterization of the generalized gradient approximation [21], using a slab geometry. The plane wave cutoff parameter $R_{MT}K_{max}$ was set to 7 and the Brillouin zone (BZ) was sampled by 9 k-points (a 3x3x1 mesh), or 100 k-points in the case of the weakly coupled Bi$_2$ and Bi$_2$Se$_3$ layers. Spin-orbit coupling (SOC) was included. For the Bi$_2$ terminated surface, a slab was constructed of 5 Bi$_2$Se$_3$ layers and 6 Bi$_2$ layers, with 10 Å of vacuum between adjacent slabs. For the Bi$_2$Se$_3$ terminated surface, a slab was constructed of 6 Bi$_2$Se$_3$ layers and 5 Bi$_2$ layers. To calculate weakly coupled Bi$_2$ and Bi$_2$Se$_3$ layers, a rhombohedral unit cell was used that retains all of the parameters of Bi$_4$Se$_3$ but with an artificial interlayer distance of 5 Å. For all cases the experimentally determined lattice parameters and atom positions were used to construct the slabs. Continuous bands were plotted by calculating the irreproducible representations of the wavefunctions at each k-point, showing which of the band intersections represent symmetry-allowed crossings. The contribution of the surface atoms to the overall
surface electronic structure was determined by calculating the partial contribution of each atomic basis set to the wavefunctions at all k-points.

The structure of Bi$_4$Se$_3$ (Fig. 1a) is composed of alternating Bi$_2$Se$_3$ and Bi$_2$ layers in a natural superlattice [22]. Bi and Se rich regions on cleaved surfaces, corresponding to Bi$_2$ bilayers and Bi$_2$Se$_3$ quintuple layers, were identified in PEEM by difference in work function (not shown). Subsequently, micro-spot x-ray photoemission spectra (micro-XPS) for the Bi 5d core level, shown in Fig. 1(b), were obtained from Bi2 and Bi2Se3 regions, respectively. The spectra taken on the Bi$_2$Se$_3$ are shifted by about 1.8eV towards higher binding energies for both components of the Bi 5d doublet. We further utilized the respective Bi 5d 5/2 component from both regions to obtain PEEM images of the surface, shown in Fig. 1(c). The terraces with different terminations are clearly visible, ranging in size from few $\mu m^2$ to $\sim (100 \mu m)^2$, comparable to the spot size in the ARPES experiments. This has proven critical for distinguishing the two different terminations and their corresponding TSSs in ARPES. The fine features in the topography measured in STM clearly reveal two types of surfaces (Figs 1(d), 1(e) and 1(f)). The topography of the region close to the step edge allows us to identify the surfaces; the measured step heights are approximately 4 Å and 8 Å, consistent with the first and the second surfaces being a Bi bilayer and Bi$_2$Se$_3$ quintuple layers respectively. The first type of surface shows atom-size dips that are $\sim$0.7 Å in depth while the second one contains mostly protrusions that are $\sim$2 Å high (Fig. 1(e)). While the exact origin of the surface defects is presently unknown, we speculate that they originate from Bi atoms that remain bonded to the Bi$_2$Se$_3$ surface during the cleaving process.

While the 60 $\mu m$ ARPES spot size is insufficient to completely resolve the two terminations, Bi- and Se-predominated surface terminations are easily distinguished, allowing for the clear determination of the surface electronic structures of both terminations. Figure 2(a) shows the ARPES spectra of the Se-rich and Bi-rich surfaces, reflecting significant differences between the two terminations. The Bi 5d and Se 3d core levels in Fig. 2(b) were measured at exactly the same locations where the ARPES spectra from Fig. 2(a) were recorded, enabling the identification of two different surface states with two terminations.

Contrary to expectations, the Bi$_2$ termination exhibits nearly linear Dirac surface states similar to those observed in topological insulators such as Bi$_2$Se$_3$, although with the hole-like dispersion, while the Bi$_2$Se$_3$ termination exhibits a non-linearly dispersing surface state. The existence of these surface states is consistent with the band inversion at $\Gamma$ for bulk Bi$_4$Se$_3$.
FIG. 1. (a) The crystal structure of the Bi$_4$Se$_3$ superlattice phase consists of alternating Bi$_2$ and Bi$_2$Se$_3$ layers. (b) Micro-XPS spectra for the Bi 5d core level, taken from Bi$_2$ and Bi$_2$Se$_3$ regions, respectively; spot size 2 micrometers (c) PEEM images obtained using respective Bi 5d 5/2 core levels showing high intensity (bright) for the Se termination (top) and for the Bi termination (bottom). (d) STM Line-cut across a step edge showing the heights of the Bi$_2$ and Bi$_2$Se$_3$ steps (4 Å and 8 Å respectively). (e) Large scale (1000 Å × 1000 Å) STM topography of the Bi$_2$ terminated surface (left) and the Bi$_2$Se$_3$ terminated surface (right). (f) False color STM topography image close to the step edge from d) where both types of surfaces can be identified (indicating a nontrival Z2 invariant) and the with the spin-chiral TSS observed earlier on Bi$_4$Se$_{2.4}$S$_{0.6}$ [23]. The calculated surface states in the Γ-M direction for the Bi$_2$Se$_3$ and Bi$_2$ terminations are shown in Figure 2(c); The circle sizes are proportional to the amount of surface character.

The calculation for the Bi$_2$Se$_3$ termination (left) shows the same type of non-linear surface state that is experimentally observed by ARPES. The calculated electronic structure indicates that the state is non-trivial; there is a symmetry-allowed crossing at about -0.5 eV and the state crosses the continuous gap in the bulk bands an odd number of times along Γ-M, therefore satisfying the odd-crossing criterion for a topological surface state. The state is similar to those states seen on the surface of topological elemental Sb [24] and on Bi$_2$Se$_3$. 
The calculated surface states for the Bi\textsubscript{2} termination (right, Figure 2(c)) clearly show a surface Dirac cone, crossing the continuous gap an odd number of times. The observed surface electronic structure bears resemblance to that found on single Bi\textsubscript{2} layers deposited on Bi\textsubscript{2}Te\textsubscript{3}, which has been suggested as a platform for quantum spin hall (QSH) edge states [17]. A close look reveals that the surface contribution vanishes precipitously upon joining the semimetallic bulk bands slightly above E\textsubscript{F}. Therefore, the surface state crosses the gap only once, satisfying the odd crossing criterion. A small continuous gap in the calculated surface state spectrum is observed at about 0.5 eV above E\textsubscript{F}.

Comparisons of the observed and calculated surface electronic structures of the Bi\textsubscript{2} and Bi\textsubscript{2}Se\textsubscript{3} terminated surfaces of Bi\textsubscript{4}Se\textsubscript{3} are shown in Figure 2(d), displaying a good match between calculation and experiment. The real crystal is slightly n-doped (by about 0.1 eV) when compared to the calculations. The global picture is that the surface states seen on the Bi\textsubscript{2} termination in Bi\textsubscript{4}Se\textsubscript{3} are similar to those seen on topological insulators such as Bi\textsubscript{2}Se\textsubscript{3}, i.e. linearly dispersive Dirac states, while those seen on the Bi\textsubscript{2}Se\textsubscript{3} termination are similar to those seen on Sb\textsuperscript{24}, i.e. highly distorted Dirac states.

To explain the overall surface state electronic structure of Bi\textsubscript{4}Se\textsubscript{3}, the calculated electronic structure was compared to those of weakly coupled Bi\textsubscript{2} and Bi\textsubscript{2}Se\textsubscript{3} layers (separated by 5 Å), shown in Figure 3(a). The weak coupling was confirmed by a lack of dispersion in Z. In the completely uncoupled case, Quantum Spin Hall edge states on the single Bi\textsubscript{2} layer would lie in the gap above E\textsubscript{F} between the valence and conduction bands of the Bi\textsubscript{2} layer. In the weak coupling case, there is a distinct band inversion between the conduction band (labelled CB\textsubscript{1, Bi\textsubscript{2}Se\textsubscript{3}}) of Bi\textsubscript{2}Se\textsubscript{3} and the valence bands (VB\textsubscript{1, Bi\textsubscript{2}} and VB\textsubscript{2, Bi\textsubscript{2}}) of Bi\textsubscript{2}, with a small SOC induced gap (about 20 meV) appearing between VB\textsubscript{1, Bi\textsubscript{2}} and CB\textsubscript{1, Bi\textsubscript{2}Se\textsubscript{3}} around E\textsubscript{F}. This is a topological band inversion; the parity of the VB\textsubscript{1, Bi\textsubscript{2}} is opposite that of both CB\textsubscript{1, Bi\textsubscript{2}Se\textsubscript{3}} and VB\textsubscript{2, Bi\textsubscript{2}}. There is also an avoided crossing gap between VB\textsubscript{2, Bi\textsubscript{2}} and CB\textsubscript{1, Bi\textsubscript{2}Se\textsubscript{3}} (about 200 meV). The Kramers point energies and dispersions of the Bi\textsubscript{2} and Bi\textsubscript{2}Se\textsubscript{3} terminated TSS correspond extremely closely to the VB\textsubscript{2, Bi\textsubscript{2}} maximum and CB\textsubscript{1, Bi\textsubscript{2}Se\textsubscript{3}} minimum, respectively, of the weakly coupled case. This suggests that the Kramers point energies of the TSS are determined by energy levels intrinsic to the individual, isolated version of the layer that hosts them.

Figure 3 (b) shows the corresponding Bi\textsubscript{2} derived features in the more realistic surface band structure that includes the full interlayer coupling. Full coupling between the layers
moves CB1$_{Bi_2Se_3}$ up in energy and the valence bands of Bi$_2$ down, retaining the band inversion at Γ but un-inverting the bands at Z in the bulk electronic structure, allowing for a nontrivial Z2 invariant. Full coupling also increases the SOC gap between CB1$_{Bi_2Se_3}$ and VB1$_{Bi_2}$, and increases the avoided crossing between CB1$_{Bi_2Se_3}$ and VB2$_{Bi_2}$ to about 0.6eV. Finally, the small gap at 0.5 eV above E$_F$ is between bands mainly derived from the Bi$_2$ and Bi$_2$Se$_3$ conduction bands and Bi$_2$ valence bands. However, all of the bands are heavily hybridized with each other; it would be interesting to see if QSH states could be hosted in that gap, as all of the involved bands have significant Bi$_2$ character.

To investigate the local spectroscopic signatures of the two surfaces and make a connection to the ARPES data we performed scanning tunneling spectroscopy of the interference patterns caused by surface defects (Fig.4). In the range of -100 mV to +100 mV we ob-
FIG. 3. (a) The calculated electronic structure of weakly coupled Bi₂ and Bi₂Se₃ layers. Heavier plotting shows the bands belonging to Bi₂. Both F and L would project to $\bar{M}$ in the surface electronic structure. (b) The calculated surface state electronic structure for the Bi₂ terminated surface of Bi₄Se₃, shown for comparison to the idealized case. Heavier plotting shows the contribution of the Bi₂ layers. Bulk bands derived mainly from Bi₂ and Bi₂Se₃ are shaded red and blue, respectively.

serve quasi-particle interference patterns on both Bi₂ and Bi₂Se₃ terminated surfaces. The Fourier transform of the real space conductance map can be linked directly to the ARPES data (Fig. 4(a) and Fig. 4(b)). The characteristic scattering vectors along the $\Gamma - \bar{M}$ direction corresponds to scattering from the inner ring-like parts of the Bi₂ surface bands close to the outer surface bands (Fig. 4(b-d)). In contrast, on the Bi₂Se₃ termination (Fig. 4(e-f)) these features are absent, consistent with the fact that the inner parts of the surface bands (marked by the dashed circle in Fig. 4(a) are indeed related to the Bi₂ surface. This further supports our band structure calculation showing that near the Fermi level only Bi₂ terminated surfaces have parts of bands close to the $\Gamma$ point (Fig. 2(c)).

On the Bi₂Se₃ surface we observe an overall suppression of the scattering intensity for vectors corresponding to surface states. This is best illustrated when the Fourier transform of the conductance map is contrasted to the joint density of states (JDOS) calculated from ARPES (see Figure 4(g-h)). The observed suppression of the scattering of the surface states
is likely due to backscattering protection coming from the spin texture, as in the case of usual topological insulator surfaces \[25\]; this is consistent with spin-resolved ARPES experiments on Bi$_4$Se$_2$S$_{0.5}$\[23\]. For comparison, Figure 4(i) shows the surface state dispersions along $\bar{\Gamma} - \bar{M}$ and $\bar{\Gamma} - \bar{K}$ that show up in the JDOS but are likely protected from backscattering. Backscattering protection in this material may not be as simple as in previously studied topological insulators since the surface bands partly overlap with the bulk bands; thus hybridization between bulk and surface bands may occur. This makes quantitative comparison between STM data and JDOS difficult even if the simple spin texture of the surface bands is assumed, and requires more detailed study. Nevertheless, the overall lack of distinct features and relatively large suppression in the Fourier transform of the conductance map suggests that the surface states are, at least partially, protected from backscattering.

In conclusion, we have shown that TSS are observed on both types of cleaved surfaces of the natural superlattice phase Bi$_4$Se$_3$. The dispersion and Kramers point energy of the TSS are shown to differ between the two surface terminations, and from simple expectations. This provides the first example of distinct TSS on different surfaces with the same crystallographic orientation in a complex material. The observations and analysis show that the electronic features of a Bi$_2$ single layer are present in Bi$_4$Se$_3$, implying that a QSH state may be hosted in the gap 0.5 eV above $E_F$. The QSH state is potentially observable by STM experiments at a simple step-edge on the surface of Bi$_4$Se$_3$, which would expose the edge of a single Bi$_2$ layer. If present, the existence of QSH states in Bi$_4$Se$_3$ would provide a unique opportunity for studying the coexistence of 1D and 2D topological electronic states in a bulk single crystal. Finally, we show that the difference in TSS in Bi$_4$Se$_3$ is due to the interaction of the building blocks; this suggests that modification of the TSS on the surfaces of topological materials may be experimentally realizable in the large family of natural superlattice materials in the Bi$_2$-Bi$_2$Se$_3$, Bi$_2$-Bi$_2$Te$_3$ and Sb$_2$-Sb$_2$Te$_3$.

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FIG. 4. (Color Online) (a) The ARPES data slice for energy $E = -100$ meV. Directions $\bar{\Gamma} - \bar{M}$ and $\bar{\Gamma} - \bar{K}$ are along $k_x$ and $k_y$, respectively. (b) Fourier transform of the STM conductance map on the Bi$_2$ terminated surface for $V = -100$ mV. The color map shows intensities from white (low) to red-black (high). The scattering vectors corresponding to the inner surface structure of the Bi bilayer to the outer bulk bands along the $\bar{\Gamma} - \bar{M}$ direction is marked by the blue and green lines. (c-f) Fourier transform of the STM conductance for various values of voltage (indicated on the top of the panels) on the Bi$_2$ surface (c-d) and Bi$_2$Se$_3$ surface (e-f). Scale bar shown in (c) corresponds to 0.2 Å$^{-1}$. (g-h) Joint density of states calculated from ARPES data for the energies $E = -75$ meV (g) and $E = 0$ meV (h). (i) ARPES map showing the fermi surface and the dispersions along $\bar{\Gamma} - \bar{M}$ and $\bar{\Gamma} - \bar{K}$.

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