Exotic Topological Insulator States and Topological Phase Transitions in Sb$_2$Se$_3$—Bi$_2$Se$_3$ Heterostructures

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Following the discovery of two-dimensional (2D) topological insulator (TI) quantum well materials,1,2 three-dimensional (3D) TI materials represent another significant novel discovery.3–7 TIs arise from strong atomic spin–orbit coupling (SOC). Strong 3D TI materials are insulating in the bulk region yet metallic on the surface boundary. The gapless boundary states, well-known as topological surface states, have exciting topological properties, such as linear dispersion and spin momentum locking,8–10 are robust against disorder, and are protected by time-reversal symmetry.4–6,11,12

Heterostructures, consisting of materials with distinct band structures, can achieve control of the electronic state and thus carrier transport, modulating the fundamental physical parameters inside the semiconductor devices such as band gap or effective mass.13,14 Exciting examples include the following: the Si/SiO$_2$ heterostructure settled the foundation for the modern semiconductor technology; GaAs/AlGaAs quantum wells, due to perfect lattice match, became promising electronic devices with well carrier confinement and high electron mobility;15–17 the quantum cascade laser, initially realized in the AlInAs/GaInAs coupled quantum well, extends the laser electromagnetic spectrum to the mid- to far-infrared portion of the electromagnetic spectrum.18

Now heterostructures are widely applied in semiconductor lasers,19 high-speed bipolar transistors,20 photonic crystals,21 and other novel electronic devices.22,23

Recently, various heterostructure-like tems composed of topological insulator and trivial materials have attracted great interest because exotic features can be induced through the interface correspondence between topologically nontrivial and topologically trivial phases, due to the existence of a topological surface state. A large number of works, based on the consideration of model Hamiltonians with variable parameters, have predicted such proximity effect induced topological properties, such as one-dimensional fermionic excitations on the dislocation line in Tl,24,25 image magnetic monopole effects on the interface between Tl and ferromagnetic materials,26

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and Majorana Fermions on the interface between TI and a s-wave superconductor.27,28 However, due to the complexity of the coupling interaction, it is still hard to unequivocally illustrate the effects of general interfacial interactions in these heterostructures. Furthermore, the real-space distribution of topological surface states is critical to the interfacial interaction, although not enough attention has been paid to this issue. Interfacial interaction can also influence the real-space distribution of topological states. Because the topological states are induced by the transition from a nontrivial to a trivial phase across the boundary, it is commonly believed that the states appear locally as 2D states near the interface on the nontrivial phase side.56–59 From the computational simulation aspect, although some works have studied the spatial distribution of topological surface states on the TI’s surface,30,31 such analysis has not been performed on heterostructures.

In this work, we investigate topological states in nontrivial–trivial heterostructures by the accurate \textit{ab initio} density functional theory approach. Bi$_2$Se$_3$ and Sb$_2$Se$_3$, possessing a similar crystal structure and lattice constant in the \textit{x}–\textit{y} plane,5,32 are chosen to construct the heterostructures. They have the rhombohedral structure with space group $D_{3d}^3(R3)$. As shown in Figure 1a, the system has a layered structure with five atomic layers as a basic unit, named a quintuple layer (QL), and the crystal structure is formed by the relatively strong covalent bond within a QL and the weak van der Waals interaction between QLs. Furthermore, the electronic structures of Sb and Bi are similar, and strong interactions near the Fermi level between Bi$_2$Se$_3$ and Sb$_2$Se$_3$ are expected. Sb and Bi belong to the same group, and Bi lies below Sb. Bi is the heaviest element with stable isotopes, and the relativistic effect causes more contraction of the outer electron shells, which greatly cancels the trend of shell expansion when going down the same group in the periodic table and results in very similar electronegativity and atomic radius with those for Sb. However, Sb$_2$Se$_3$ is a trivial insulator, whereas Bi$_2$Se$_3$ is a topological insulator due to much stronger SOC effect in Bi atoms.5,30

**RESULTS AND DISCUSSION**

First, we computed the electronic band structures for Bi$_2$Se$_3$ and Sb$_2$Se$_3$ as a reference to confirm their topological nature. Eight QL (∼8 nm thick) nanoslabs, which are thick enough to avoid considerable coupling between the top and bottom surface, were used.33,34 For the Bi$_2$Se$_3$ nanoslab (Figure 1b), a linearly dispersive Dirac cone with a Dirac point at the $\Gamma$ point ($B_1 + B_2$ for Bi$_2$Se$_3$, $S_1 + S_2$ for Sb$_2$Se$_3$, and $I_1 + I_2$ for In$_2$Se$_3$). The dashed vertical lines separate the top or bottom quintuple layer from the inner region.

![Figure 1. Comparison between Bi$_2$Se$_3$, Sb$_2$Se$_3$, and In$_2$Se$_3$. (a) Layered Bi$_2$Se$_3$ or Sb$_2$Se$_3$ crystal structure. Bi (or Sb) atoms and Se atoms are marked by red and purple balls, respectively. (a,c) Lattice constants in the hexagonal cell. (b–d) Band structures for 8 QL Bi$_2$Se$_3$, Sb$_2$Se$_3$, and In$_2$Se$_3$ nanoslabs, and the dashed horizontal line shows the position of Fermi energy. (e–g) Closest to Fermi real-space charge density of the states (RDOS). The RDOS is defined as charge density integration of a state on $x$–$y$ plane at the specified depth $z$: $P(z) = \int |\psi(x, y, z)|^2 \, dx \, dy$. Here, closest to Fermi RDOS is the summations of RDOS for the highest valence state and lowest conduction state at $\Gamma$ point ($B_1 + B_2$ for Bi$_2$Se$_3$, $S_1 + S_2$ for Sb$_2$Se$_3$, and $I_1 + I_2$ for In$_2$Se$_3$). The dashed vertical lines separate the top or bottom quintuple layer from the inner region.](image-url)
2 nm in depth from the surface. Interestingly, the density peaks appear at the Bi atoms, presumably due to the strong SOC effect of Bi atoms. In contrast, the closest to Fermi states, S1 and S2, in Sb2Se3 (Figure 1f) are not real surface states, and the charge density is nonzero even in the middle of the slab far from the surface. Therefore, the RDOS shape can be viewed as a reasonable characterization method for the real-space properties of the topological surface state. In the following study, this method will be repeatedly applied to study the topologically non-trivial property and visualize the real-space density distribution.

We simulated four types of Sb2Se3–Bi2Se3 heterostructured slabs with one, two, three, and six Sb2Se3 QLs on the top and bottom surfaces of six Bi2Se3 QLs. It has been demonstrated, both theoretically and experimentally, that a slab with six QLs of Bi2Se3 alone has a gapless Dirac cone. As shown in Figure 2a,d,f,i, the gapless surface states exist for all four types of heterostructured slabs, which indicates that the topologically nontrivial slabs do not disappear when coating Sb2Se3 (trivial insulator) onto Bi2Se3 (nontrivial insulator). This is expected because the time-reversal symmetry is not violated. However, it is surprising when looking at the real-space distribution of topological states (Figure 2c,e,h,j). The topological states always concentrate inside the trivial Sb2Se3 slabs, as shown by the topological RDOS curves. The dominant concentration of topological states in Sb2Se3 QLs is true for all four types of heterostructured slabs with different thicknesses of Sb2Se3. When coating 1 QL of Sb2Se3 on both surfaces (Figure 2c), the shape of charge density is similar to that in uncoated Bi2Se3, although the largest peaks locate at the Sb atoms instead of Bi atoms. For 2 QLs (~2 nm), 3 QLs (~3 nm), and 6 QLs (~6 nm) of Sb2Se3 coating (Figure 2e,h,j), the surface states spread throughout the entire region of the Sb2Se3 slabs and extend very little into the Bi2Se3 region. Compared to slabs of Bi2Se3 alone, where the 2D topological states are distributed only within 2 QLs (~2 nm) below the surface and are truly "surface states", the heterostructures show two surprising properties of their topological states. First, there exists a quantum topological phase transition, in which trivial Sb2Se3 transforms into the nontrivial phase and nontrivial Bi2Se3 transforms reversibly into the trivial phase. Second, to the extent of 6 QL Sb2Se3 coatings, the topological states in the heterostructures are distributed "bulk-like" instead of localizing only at the surface.

To determine whether the gapless states inside the Sb2Se3 layers of heterostructures have topological nature, we also calculated the spin polarization in the Dirac cone, which is the strongest evidence of nontrivial topological character.19–21,30 Figure 2b,g shows the spin orientation on the gapless states in the 1 QL and 3 QL Sb2Se3 coating cases. It can be found that the equal energy surface and spin textures for two states are quite similar. Both energy surfaces are nearly perfect circles; the spin lies in the plane; while moving around the Fermi surface, the spin orientation rotates simultaneously, forming a left-handed spin–orbit ring. Therefore, despite the dramatic quantum topological phase transition in heterostructures, the topological states retain all of the characteristics of the topological Dirac cone.

To elucidate the origin of the surprising topological insulator states in Sb2Se3–Bi2Se3 heterostructures, we carried out comparative studies on In2Se3–Bi2Se3–In2Se3 heterostructures. As shown in Figure 1d,g, In2Se3 is a trivial insulator with the same crystal structure as Bi2Se3 and Sb2Se3. When coating 1 QL, 2 QL, and 3 QL In2Se3 on the surfaces of Bi2Se3, the gapless topological state always exists (Figure 3a,c,e). For all cases (Figure 3b,d,f), the wave functions of the surface states concentrate in the top QL and bottom QL of the Bi2Se3 slab, penetrating only slightly into the In2Se3 regions. In contrast to Sb2Se3–Bi2Se3–Sb2Se3, the topological states of In2Se3–Bi2Se3–In2Se3 heterostructures are only ordinary topological interface states with similar nature to the Bi2Se3 surface states (the vacuum–Bi2Se3 interface states).

To understand the fundamental distinction between these two heterostructures, we analyze the near-Γ atomic orbital partial density state in energy space (PDOS, defined in the caption of Figure 4). We qualitatively studied characteristics of band states near the Fermi energy in three kinds of heterojunctions: (a) 3 QL Sb2Se3 coated Bi2Se3 (3S–B junction); (b) decoupled 3 QL Sb2Se3 coated Bi2Se3 (d3S–B junction), where the width of the van der Waals gap between Sb2Se3 and Bi2Se3 is artificially extended from the equilibrium length d ~ 2.5 Å to a larger one d ~ 3.0 Å in order to weaken the interaction between two materials; (c) 3 QL In2Se3 coated Bi2Se3 (3I–B junction). In the decoupled d3S–B junction, as shown in the RDOS curve in Figure 4f, the topological state remains in the Bi2Se3 region, similar to the vacuum–Bi2Se3 systems, which indicates that a topological phase transition takes place when the interaction between Sb2Se3 and Bi2Se3 increases. Therefore, 3S–B and d3S–B junctions can serve as good models to study the mechanism of topological phase transitions. Without the SOC effect in either 3S–B (Figure 4a) or d3S–B (Figure 4d) junctions, the Se orbital with negative parity occupies the top of valence band region, and Bi and Sb orbitals with positive parity occupy the bottom of conduction band region. In the d3S–B heterojunction (Figure 4d), when Sb2Se3 and Bi2Se3 decouple, the Se orbital in Bi2Se3 (labeled as Se1) sits on the top of the valence band while the Se orbital in Sb2Se3 (labeled Se2) locates below it, and the near-Fermi level orbital forms a Se2–Se1–Bi–Bi orr. However, in the 3S–B junction (Figure 4a), when Sb2Se3 and Bi2Se3 couple, the Se1
and Se2 orbitals strongly interact and the Se2 orbital dominates the edge of the valence band, so the state order changes to Se1—Se2—Sb—Bi. By turning on the SOC effect, band inversion occurs between the Bi and...
Se states (Figure 4b,e), so the sign of total parity for all of the occupied bands changes, and the system transfers into a topological nontrivial phase. However, the variance of the near-Fermi band structure due to Sb2Se3—Bi2Se3 interaction can lead to distinct band inversion pictures, as shown in Figure 4c,g. In the d3S—B decoupled junction, the Se1 state from Bi2Se3 becomes the conduction band (Figure 4e). Bi2Se3 and Sb2Se3 retain their topologically trivial and nontrivial nature, respectively. In contrast, for the 3S—C coupled junction, the Se2 state from Sb2Se3 rises to the conduction band (Figure 4b). The parity for Sb2Se3 becomes negative, while that for Bi2Se3 becomes positive. Therefore, the roles of the two materials exchange and the topological phase transition happens.

For the In2Se3—Bi2Se3 heterojunction, the situation is completely different (Figure 4h—j). The Se orbital (labeled Se3) and the In orbital of In2Se3 locate far from the Se1 and Bi orbitals of Bi2Se3 (Figure 4h,i). The coupling between Se3 and Se1 or between In and Bi is very weak. Therefore, In2Se3 coating has little influence on the topological property, and the band inversion picture is similar to the vacuum—Bi2Se3 system (Figure 4j).

The detailed mechanism of the “bulk-like” state exceeds the capability of ab initio simulation. A possible reason is that the Bi and Se2 states involved in the band inversion locate in different materials. On one hand, Sb2Se3 is in a nontrivial phase, so the topological state exists and crosses the vacuum—Sb2Se3 interface.

Figure 3. Topological surface state in In2Se3—Bi2Se3—In2Se3 sandwich slabs with different In2Se3 thickness. (a,c,e) Band structures with one, two, and three In2Se3 quintuple layers on each surface of Bi2Se3 slabs, respectively, and the corresponding Bi2Se3 slabs in the middle are with six QLs. (b,d,f) Closest to Fermi RDOS for these sandwich slabs. The black dashed vertical lines are the boundaries between In2Se3 and Bi2Se3, and the regions between black and red dashed lines are the top and bottom QLs in the Bi2Se3 slab. The green and blue bars represent the In2Se3 and Bi2Se3 slab regions, respectively.
On the other hand, due to strong coupling and the spatially mismatched band inversion, the topological state will be a mixture of all the bulk orbital states near the Fermi level, \( |Sb_{\text{se2}} \rangle \) and \( |Sb_{\text{se1}} \rangle \) on the conduction band and \( |Bi_{\text{bi}} \rangle \) and \( |Se_{\text{bi1}} \rangle \) on valence band, which indicates that this state has a real-space distribution in both materials. Therefore, this state should spread across the whole region of Sb\(_2\)Se\(_3\) slabs. The detailed theoretical research, using an analytic method, is ongoing.

**CONCLUSIONS**

In conclusion, we have investigated Sb\(_2\)Se\(_3\)/C0Bi\(_2\)Se\(_3\) heterostructures. Topological states migrate from nontrivial Bi\(_2\)Se\(_3\) to trivial Sb\(_2\)Se\(_3\), and surprising topological states with bulk-like spatial distribution were discovered, even when the thickness of Sb\(_2\)Se\(_3\) extends to \( \sim 6 \) nm. These states are distinct from topological surface states. Our results change the existing viewpoint that the topological surface state always appears locally at the interface within a couple of QLs between the trivial and nontrivial phase and shows an example of exotic phenomenon in TI-based heterostructures. On the other hand, the deformability and expansibility of the topological state will also give inspiration to experiment, such as in electronic devices, because the surface or boundary restriction can be eliminated, and the exciting features related to this state can be utilized in a wider range.

**COMPUTATIONAL METHODS**

All of the simulation systems are slab geometry. Fully self-consistent first-principle calculations, including atomic spin–orbit coupling, were performed using the Vienna Ab Initio Simulation Package (VASP) in the framework of density functional theory (DFT).\(^3\)\(^5\)\(^6\) The projector-augmented wave (PAW) pseudopotential\(^7\) was adapted, and the GGA exchange-correlation function was described by Perdew–Burke–Ernzerhof (PBE).\(^8\) To ensure convergence, we used 350 eV for the
cutoff energy of the plane-wave basis. The vacuum area with a thickness of more than 20 Å was used to separate the periodic images in the z-direction, which is wide enough to avoid any artificial interaction between images after our tests. All of the nanolabs are infinite and periodic in the x-, y-, and z-directions. The lattice constants for Bi$_2$Se$_3$ and In$_2$Se$_3$ are taken from experimental data, and the lattice mismatch and the weak van der Waals interaction between QLs suggest that the Bi$_2$Se$_3$ lattice mismatch and the weak van der Waals interaction between QLs suggest that the Bi$_2$Se$_3$ and In$_2$Se$_3$ heterostructures should have little lattice stress and can serve as good model systems for our investigation. For the heterojunction simulations, the in-plane lattice constants are chosen as that of Bi$_2$Se$_3$, $a = 4.138$ Å.

For slab systems, the Brillouin zone (BZ) is two-dimensional, and there are three non-equivalent time-reversal invariant momentum (TRIM) points (0, 0), (π, 0), and (π, π). The vacuum area with a thickness of more than 20 Å was used to separate the periodic structures partial support from National Nanotechnology Infrastructure Network (NINNI).

**REFERENCES AND NOTES**