Thin films of topological crystalline insulator SnTe in contact with heterogeneous atomic layers

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Abstract
Tin telluride is a topological crystalline insulator that has gapless surface states protected by mirror symmetry. The symmetry remains intact when the insulator is reduced in thickness and becomes a thin film, according to ab initio calculations based on density functional theory. Furthermore, a SnTe thin film in contact with a heterogeneous atomic layer is capable of closing energy gap caused by quantum tunneling between the two thin film surfaces and therefore distinguishes two conducting channels through surface and interface states respectively. Our calculations of SnTe films deposited with a lead telluride layer have two Dirac cones separated in energy, while the same film in contact with strontium telluride have the cones separated in momentum. The composite with a magnetic manganese telluride layer, however, loses both the mirror and time-reversal symmetry.

1. Introduction
Topological insulators (TIs) [1–6] have been predicted to provide exotic applications in future generations of nanoelectronics and are themselves of important fundamental values in physics. Surface states of TIs are typically characterized by the presence of Dirac cones in the energy gap of the bulk electronic band structure. The linear crossing bands and the chiral spin texture possess time-reversal symmetry that ensures non-dissipative transport in defiance of the presence of impurity atoms and geometric perturbations. A variety of interesting and fundamental physics can therefore be exploited, including quantum spin Hall effects [7–11] and the elusive quasiparticle-like Majorana fermions [12]. Potential applications in lossless transport, spintronics, and quantum computing offer more incentives for searching new and more easily synthesized and readily integrated topological materials. Topological crystalline insulators (TCIs) [13] are a relatively new comer in this line of development. Energy bands of TCIs have the protection of mirror symmetry of the crystals that can be characterized by a non-zero mirror Chern number. Tin telluride, for example, is one typical TCI that has been predicted by theoretical calculations and confirmed by experiments [14–16]. To further understand the feasibility of using SnTe as a nano-scale electronic component, a theoretical probe into how SnTe behaves as it is reduced in size along at least one dimension is very helpful. Whether thin films of SnTe get to retain the topological properties of their thicker (bulk) counterparts is an important and practical problem.

SnTe has the rock-salt crystal structure with numerous symmetry surfaces. Its surface states on the [001] surface, for example, have been shown to possess two Dirac cones centered along the line connecting the symmetry point $\bar{X}$ through $\Gamma$ to $-\bar{X}$ in the surface Brillouin zone (illustrated in figure 1(a)), in accordance with the mirror Chern number. The line is also the intersection of the [110] mirror plane with the surface. In contrast to a $Z_2$ TI having only one single Dirac cone at the zone center, states of the SnTe [001] surface are duly protected by reflection symmetry as specified by the mirror plane.

2. Method
We use spin-polarized density-functional calculations as implemented in the Vienna ab initio simulation package [17, 18] to derive all electronic bands. For exchange-correlation functional the version of Perdew, Burke...
and Ernzerhof [19] is adopted. The electron–ion interaction is represented by the projector-augmented wave potential. Cutoff energy for the expansion of wave functions and potentials in the plane-wave basis is chosen to be between 300 and 500 eV, depending on the choice of the specific heterogeneous layer. Complete relaxation of the combined structure including lattice constants are executed with a \( 9 \times 9 \times 1 \) sampling of the first Brillouin zone. Vacuum space in the supercell is allocated by setting a minimum height of 15 Å perpendicular to the thin film in the cell, which proves large enough to minimize artificial interactions between supercells. Bader charge analysis [20] is used to calculate charge transfers between atoms.

3. Results

Our calculations begin with a 10-layer SnTe and obtain a relatively large band gap around 105 meV along the \( \Gamma \rightarrow \bar{X} \) direction as shown in figure 1(b), indicating a pronounced quantum tunneling effect between the two surfaces of the film. The gap can be reduced if the film grows thicker and the tunneling effect accordingly diminishes. In figures 1(e) and (f), for example, the 30-layer SnTe has an energy gap of only 14.3 meV while the gap for the 33-layer film is less than 10 meV. Shown in figure 2(a) is a blowup of the energy bands for the 30-layer film close to the \( \bar{X} \) point near the surface Brillouin zone boundary. It distinguishes more clearly two almost degenerate bands contributed overwhelmingly by atoms in each of the two surface layers. Starting from the \( \mathbf{k} \) point at \((0.45, 0, 0)\), in unit of \( 2\pi/a \) with \( a \) being the lattice constant, the top valence band is made mostly of the \( p \) orbitals from Te atoms in the surface layer of the film. The band reaches its maximum energy and then goes downward, changing its composition to mostly \( p \) orbitals from Sn atoms of the same layer, all the way to \( \bar{X} \), where two surface valence bands converge. Furthermore, figure 2(b) offers a partial two-dimensional scan of energy in the \( k_x-k_y \) plane of the highest energy surface states below the energy gap. Spin texture as represented by arrows assigned to \( k \) points manifests reflection symmetry about the mirror plane. The flip of spins at \((0.466, 0)\) is another indication of the valence band reaching the band maximum.

![Figure 1. Energy band evolution of SnTe thin films along symmetry directions, as specified in (a) the first Brillouin zone and surface Brillouin zone of SnTe. One mirror plane is also presented. Band gaps of SnTe thin films shrink from (b) 105 meV for a 10-layer film, (c) 39.8 meV for 20 layers, (d) 17.0 meV for 25 layers, (e) 14.3 meV for 30 layers, to (f) 9.90 meV for 33 layers. Shaded areas are projections of SnTe bulk energy bands.](image-url)
Although surface band gaps can be closed and Dirac cones formed for thick SnTe films, thinner films are more readily synthesized and more flexible for integration into nano-scale two-dimensional devices. The problem of quantum tunneling between the two surfaces of thinner films due to their stronger coupling can be overcome by impurity doping in one of the surface layer or by placing the film in contact with a heterogeneous atomic layer or substrate [21–23], thus removing the degeneracy of the two surfaces. The surface interacting with impurity atoms or heterogeneous layers tends to shift its energy levels away from those of the pristine surface, and in turn makes tunneling more difficult.

We first consider the interaction between a SnTe film and a PbTe layer. Bulk PbTe has the same crystal structure as SnTe, with a lattice constant \((6.454 \, \text{Å})\) only slightly larger than that of SnTe \((6.310 \, \text{Å})\). A layer of PbTe deposited on SnTe, as is shown in figure 3(a) for a 19-layer substrate, causes no appreciable change of the substrate lattice, according to our DFT calculation that takes into account structure relaxations and spin–orbit interaction. There is no longer an energy gap as associated with the thin pure SnTe film, since interaction between the PbTe layer and the substrate destroys inversion symmetry in the direction perpendicular to the surface and lifts degeneracy of the surface bands, separating those associated with the deposition of the heterogeneous layer from those remaining pristine. Moreover, two Dirac cones are identified (figures 3(b) and (c)) along the \(\Gamma – X\) direction with spin polarization (marked as crosses and circles in figure 3(c)), one with its Dirac point at \((0.468, 0)\) is 0.0790 eV above the Fermi level and another at \((0.453, 0)\) is 0.0229 eV below the Fermi level, indicating an increase of 14.2 meV in energy separation as compared with the previous case. As figure 4(c) shows, the two cones can be schematically represented by four crossing linear bands. Each band is identified with its spin polarization directed either along \(y\) or \(-y\) direction. Analysis of the compositions of the two cones reveals that the upper cone is associated with the pristine surface as it is overwhelmingly populated by electronic states of the surface atoms, with Te \(p_x\) and Sn \(s\) orbitals for the \(y\) band with spin directed along \(y\) direction, and Sn \(p_x, \) Sn \(p_y, \) and Te \(s\) orbitals for the \((-y)\) band with spin pointing toward \(-y\). The lower cone, on the other hand, is comprised mostly of the impurity Pb atoms and others at the interface. Pb atoms, for example, dominate the presence in the band of the lower cone associated with spin in \(y\) direction.

**Figure 2.** A close-up look at energy bands of the 30-layer SnTe film and energy–momentum topography with spin texture. (a) Energy bands are drawn from \((0.45, 0)\) to \(X\) in unit of \(2\pi/a\). Each of the two nearly degenerate bands corresponds to one individual surface of the film. (b) Energy–momentum topography is mapped out for the shown energy window at right, and arrows are used to specify spin directions. Mirror symmetry is evident in the picture.
Even though PbTe is not a TCI under ambient conditions, a single layer of PbTe deposited on the SnTe film does not disturb the mirror symmetry. Energy-momentum topography (figures 4(d) and (e)) is plotted for part of the above four linear crossing bands, with energy ranging from $-0.09$ to $0.05$ eV, $k_x$ from $(0.4, 0)$ to $(0.6, 0)$, and $k_y$ from $(0, -0.025)$ to $(0, 0.025)$. It is clear that all electronic states continue to be protected by the reflection symmetry with respect to the plane along the $\bar{\Gamma} - \bar{X}$ direction. The figure also reveals that time-reversal symmetry provides additional protection for electron transport. Energy of the electron with momentum $k$ and its locked spin, for example, is equal to energy of the electron with momentum $-k$ (after being translated by a reciprocal lattice vector if necessary) and opposite spin, constituting a Kramers pair of electrons. Backward scattering is therefore greatly diminished.

We next turn to another heterogeneous layer of atoms and see if its deposition produces similar results. Bulk SrTe has also the same crystal structure as SnTe and PbTe, with a slightly larger lattice constant ($6.47$ Å) than either of the two. Based on our calculation, a single layer of SrTe deposited on 29 layers of SnTe, does not change the lattice constant of SnTe in any significant manner. Its interaction with the SnTe substrate is also comparable to that of PbTe. Binding energy $E_B$ between a heterogeneous layer XTe and its SnTe substrate is calculated from the formula $E_B = E(XSnTe) - E(SnTe) - E(XTe)$, where $E(XSnTe)$ represents the total energy of the composite film and $E(SnTe)$ and $E(XTe)$ each represents the total energy of one of its two constituents. Based on the formula, binding between the PbTe layer and the 29-layer SnTe is found to be $-0.865$ eV per unit cell, only slightly stronger than the value of $-0.758$ eV for the SrTe on 29-layer SnTe. Analysis of charge transfer, however, indicates that the PbTe layer attracts electrons from the SnTe substrate while SrTe does the opposite. This contributes to different relative positions of the two Dirac cones for SrTe deposition as compared with the PbTe deposition.

Shown in figures 5(a) and (b) are energy bands of SrTe + 29 SnTe, two Dirac cones are also present along the $\bar{\Gamma} - \bar{X}$ direction, connecting the valence and conduction bands. Instead of a vertical separation in energy as in
the PbTe deposition, the two cones are now conspicuously separated in crystal momentum and have about the same energy value for the Dirac points. The cone closer to the Brillouin zone boundary is associated with the interface and impurity atoms and has its tip exactly at the Fermi level while the cone associated with pure SnTe surface is about $0.023 (2\pi/a)$ to the left, with its tip slightly above the Fermi level. With only two valence electrons available for each Sr atom and charge transfer to the SnTe substrate, the cone for the heterointerface atoms is shifted upward in energy relative to the other until both are almost on a par. Four crossing bands with their associated spins are depicted schematically in figure 5(c) to isolate the effect of this type of heterogeneous contact. The left Dirac cone, which is associated with the pure SnTe surface, has the same composition as its counterpart in PbTe + 29 SnTe. The right cone, however, consists mostly of Sn $s$ and $p$ orbitals. Due to fewer valence electrons provided by Sr and strong charge transfer, energy levels contributed by Sr electrons can only be found 1.5 eV below the Fermi level. Energy-momentum topography (figure 5(d)) with spin texture is also provided for energy bands near the Fermi level. It also shows reflection symmetry on both sides of the mirror plane and time-reversal symmetry of $k$ points by extension into the second Brillouin zone just like the deposition of PbTe layer.

Figure 4. A layer of PbTe deposited on 29-layer SnTe substrate. (a) Two Dirac cones connecting valence and conduction bands are found in bulk band gap. (b) Extending the plot into the second Brillouin zone, the two sets of Dirac cones are shown to conserve time-reversal symmetry. Size of the Cross (circle) indicates magnitude of spin polarization in $y$ ($-y$) direction. (c) The two Dirac cones are separated by energy as indicated by the schematic crossing bands with solid (dashed) and black (blue) line representing energy band in upper (lower) cone and spin polarized in $y$ ($-y$) direction. Energy-momentum topography within the specified energy window is shown in (d) and (e) separately for part of the first and second Brillouin zone. Arrows are used to indicate spin directions.
Transport for either PbTe + 29 SnTe or SrTe + 29 SnTe is dominated by the two Dirac cones of electronic states near the Fermi level. With an adjustable bias, the interface and pure surface each carries a current with its provenance easily identified due to the separation of film thickness. On the other hand, the total spin current is zero, because the two charge currents carry opposite spins. Transport is especially robust because mirror symmetry provides extra protection against backward scattering of electrons in addition to the time-reversal symmetry.

Properties of SnTe in contact with a magnetic atomic layer are quite different from aforementioned results. Consider a MnTe layer deposited on the same 29 layers of SnTe. It is known that magnetism destroys time-reversal symmetry. But calculation also shows that mirror symmetry disappears as a result. Firstly, Dirac cones are destroyed as is evident in figures 6(a) and (b), where one is completely dissolved due to the contact of the magnetic MnTe layer, and the remaining crossing bands associated with the pristine surface are topologically trivial. Furthermore, z components of spins now emerge, in addition to the x and y components shown in the energy-momentum topography (figure 6(c)) for energy values close to the Fermi level, they are specifically labeled with numerical magnitudes in figure 6(d). On both sides of the mirror plane parallel spin components in the positive z direction indicate that mirror symmetry no longer exists. Also gone is transport protected by time-reversal and mirror symmetry.

Figure 5. A layer of SrTe deposited on 29-layer SnTe substrate. (a) Two Dirac cones connecting valence and conduction bands are also found in bulk band gap. (b) Extending the plot into the second Brillouin zone, the two sets of Dirac cones are shown to conserve time-reversal symmetry. Size of the cross (circle) indicates magnitude of spin polarization in y (−y) direction. (c) The two Dirac cones are separated by momentum as indicated by the schematic crossing bands with solid (dashed) and black (blue) line representing energy band in upper (lower) cone and spin polarized in y (−y) direction. (d) Energy-momentum topography within the specified energy window is shown in part of the first and second Brillouin zone. Arrows are used to indicate spin directions.
4. Conclusion

In summary, SnTe thin films deposited with a layer of non-magnetic heterogeneous atomic layer are able to maintain their mirror symmetry. Two Dirac cones are separated by the contact and can be shifted either in energy as in the case of a PbTe layer or in momentum by a SrTe layer. Currents that are protected by the mirror symmetry as well as the time-reversal symmetry are carried by electrons from the heterointerface atoms and atoms of the pristine surface respectively. However, any contact with a layer containing magnetic atoms will destroy Dirac cones and all associated symmetries. The results should find application in nano-scale circuits that utilize topological surface conductions.

Acknowledgments

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