Topological states of Sb thin films contacted by a single sheet of heterogeneous atoms

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Abstract
We found that thin antimony films contacted by a single layer of a variety of atoms can form topological surface and interface states in the gap of bulk energy bands that preserve time-reversal symmetry. Using density functional calculation, we have included bismuth, graphene, boron-nitride and boron-doped graphene layers in our investigation. In most cases, Dirac cones are found in the band structures and spin textures indicate no back scattering of conduction electrons. In the case of a BC$_3$ layer deposited on an Sb film as thin as three bilayers, a Dirac cone consisting mostly of interface states is formed close to the Fermi level. If the composite is gated by an adjustable voltage, electron transport can switch between two modes of opposite spins, and between one or two modes of 100% spin polarization. The results should be very useful in the applications of topological conduction and spintronics.

Keywords: topological insulator, Sb thin film, Dirac cone, spin texture

1. Introduction

Topological insulators [1–10] have conducting surface states that are separated from the insulating bulk states. The surface states form Dirac cones with time-reversal symmetry in the energy gap of the bulk electronic bands. The directions of their associated crystal momenta are
locked to the electron spins in a way that prevents back scattering of electrons irrespective of the presence of non-magnetic impurities or geometric disturbances. Topological insulators are very valuable in applications requiring non-dissipative or spin-polarized transports. In this regard, an important question concerns the physical sizes of topological insulators. If a topological insulator is to be integrated into a nanoscale circuit, it has to be shrunk in at least one dimension. However, there is a limit on how far the topological insulator can be reduced. Below a certain thickness quantum tunneling between the two surfaces of a free-standing film would open a gap and destroy the Dirac cone [10].

A thin film deposited on a substrate, however, may circumvent the effect of the tunneling between the two surfaces of the film. Although a free-standing four-bilayer Sb (111) film has a large tunneling-induced energy gap, the same film supported by a Bi-terminated silicon substrate forms a Dirac cone at the Brillouin zone center, as was demonstrated by the angle-resolved photoemission experiment [11]. The thin Sb film [11–13] in contact with heterogeneous atoms in the substrate can be simulated theoretically as an adsorption of impurity atoms on one film surface. According to calculations based on density functional theory (DFT), there is substantial charge transfer between the adsorbed hydrogen or non-magnetic transition-metal atoms and the film, and the energy gap is closed as a result [11, 14]. In order to better understand the interaction between thin films of a topological insulator and their substrate, we set out to investigate the electronic structure of the Sb film deposited on a layer of heterogeneous atoms. Bonding between the film and the layer and the interface states formed as a result should offer useful information about the feasibility of producing topological conduction for such configurations, which are more realistic in practice and can be used in more general applications.

2. Method

Our first calculation dealt with Sb (111) films in contact with a single layer of Bi. We used the VASP [15, 16] codes for this and subsequent calculations. General features included spin–orbit interaction, local density approximation for exchange–correlation functionals, and a cutoff energy of 400 eV for expanded plane waves. Sampling of the Brillouin zone was usually done with a $9 \times 9 \times 1$ mesh of $k$ points. Relaxation of atomic positions to minimize the strain was always executed before the calculation of energy bands. The vacuum layer for the relaxation process has a height of 18 Å perpendicular to the surface.

3. Results

Figure 1(a) shows the calculated energy bands of a four-bilayer Sb (111) film in contact with a single layer of Bi, where a primitive cell consisting of eight Sb and two Bi atoms was used. As the experiment [11] has shown, a Dirac cone at approximately 0.30 eV below the Fermi level is formed in the gap of the projected bulk energy bands represented by shaded areas. The states of the cone are mostly made of electrons from the surface not in contact with Bi. Not surprisingly, Dirac cones also form in Sb films having more bilayers. Figure 1(b) gives the band structure of a five-bilayer Sb (111) film in contact with a Bi layer, and figure 1(c) stands for that of a six-bilayer Sb film. It is clear that increasing Sb layers does not change the fact that a Dirac cone exits in the gap region of bulk Sb. A more interesting question is whether the film can be shrunk
Figure 1. Energy bands along the $\bar{\Gamma} - \bar{M}$ direction of a (a) four-bilayer, (b) five-bilayer, (c) six-bilayer, and (d) three-bilayer Sb (111) film in contact with a single layer of Bi atoms.
further. Band structure in figure 1(d) indicates that a three-bilayer Sb (111) film in contact with the Bi layer is also capable of producing a Dirac cone, located at about 0.33 eV below the Fermi level. Not only that, even if the Bi layer has vacancy defects, the whole structure is still able to produce Dirac cones and topological conduction. Two types of vacancy defects were investigated for the purpose. In order to accommodate the defects a much larger unit cell containing 24 Sb atoms from the three-bilayer Sb (111) film was used. In figure 2(a) a layer of Bi that is greatly distorted due to some absent Bi atoms is shown over the Sb (111) film. A Dirac cone is still preserved in the gap of projected bulk bands of Sb. Also shown is the spin texture [17] in the $k_x-k_y$ plane at 0.28 eV below the Fermi level. Two equi-energy circles presenting spin-locked crystal momentum vectors confirm time-reversal symmetry. Another
distribution of defects results in the less distorted Bi layer shown in figure 2(b), where a Dirac cone and its associated spin texture at -0.19 eV are also drawn. It is obvious that defects in the Bi layer are not a factor affecting topological conduction of the composite structure. This is certainly consistent with the calculation involving isolated impurity adsorptions of Sb films. These results reveal the flexible role Sb thin films assume in topological conduction if the films come into contact with a layer of heterogeneous atoms. It should be stressed that we continue to use the term ‘topological conduction’ here and thereafter as an extension of the description of the bulk topological insulator Sb.

We would like to exploit further the capability of the three-bilayer Sb (111) film, which is probably the lower limit in thickness for most applications in topological transport, by placing it in contact with other materials. Graphene in particular is made up of a single layer of carbon atoms, and the deposition of such light atoms on the Sb film was the target of our next investigation. We employed the same large unit cell as was used in the investigation of the distorted Bi adlayer contact, consisting of 24 Sb atoms from the three-bilayer Sb film and 24 C atoms from graphene. There were, however, several possible configurations for the composite structure. An Sb atom can occur directly over a C atom (top site), perch on the middle point of the bond between two C atoms (bridge site), or sit right on the center of the hexagon of C atoms (hollow site). Calculation indicated that the configuration with Sb atoms at hollow sites is energetically most favorable, followed by the bridge-site contact. Binding energies (per unit cell) for the three configurations, given in table 1, differ little from one another. Band structures, however, show more distinct features for each of the three configurations. Overall, the Dirac cone of a free-standing graphene is folded back to the Brillouin zone center as a result of the deposition, as is shown in figures 3(a)–(c), corresponding to bridge, hollow, and top site binding, respectively. Although the binding with the Sb film is relatively weak, it is enough to generate an energy gap between the two tips of the cones due to uneven interaction between the C and Sb atoms, with some C atoms being closer to Sb than others. Interestingly, it is the two weaker bindings that produce Rashba spin splitting in the energy bands, as in figures 3(a) and (c). The bands with blue circles are largely made of electrons from interface Sb and C atoms. Apparently, Sb atoms at bridge sites or on top of C atoms interact with C more strongly and result in more splitting of energy bands. Bands with black circles are mostly from Sb atoms on the other surface of the film.

If one substitutes boron atoms for some of the C atoms in the graphene layer, different electronic structures are expected due to the change in bonding and different number of valence electrons. As an example we display five calculated energy bands in figure 4, along the $\bar{\Gamma} - \bar{M}$

| Layer contact          | $E_b$ (eV) | Electrons transferred to the layer contact (e) |
|------------------------|------------|-----------------------------------------------|
| Graphene (bridge sites)| −0.467     | 0.124                                         |
| Graphene (hollow sites)| −0.512     | 0.138                                         |
| Graphene (top sites)   | −0.444     | 0.136                                         |
| BC3 (bridge sites)     | −1.452     | 0.630                                         |
| BC3 (hollow sites)     | −0.991     | 0.462                                         |
| BC3 (top sites)        | −1.394     | 0.550                                         |
| BN (top sites)         | −0.492     | 0.084                                         |
direction in the first Brillouin zone, of a three-bilayer Sb (111) film in top-site contact with a B-doped graphene sheet, with the latter evolving from a lower concentration of B (1/24) to BC$_3$. The increase in B atoms alters the shapes and distributions of bands and realigns the position of the Fermi level accordingly. Dirac cones, nonetheless, are present in all five configurations. In the case of BC$_3$ contact, for example, two Dirac cones are present and two energy values are chosen for spin texture analysis. For 0.07 eV above the Fermi level two equi-energy circles in the $k_x-k_y$ plane are shown in figure 5(a), with the inner one corresponding to states mostly contributed by Sb atoms (blue circles in figure 4(e)) at the interface and the outer one
Figure 4. (a)–(e) Evolution of energy bands of a three-bilayer Sb (111) film in top-site contact with B-doped graphene from the concentration of 1/24 to BC$_3$. Blue (black) circles in (e) indicate contribution from interface (pristine surface) electrons.
representing states largely from the other surface of the Sb film. Both energy circles are spin-polarized and have spin direction perpendicular to the electron momentum. At 0.14 eV below the Fermi level, two equi-energy circles on the $k_x - k_y$ plane are also present (figure 5(b)). However, spin directions are reversed at $k$ points in each energy circle of the cone relative to those of figure 5(a), and states are mostly made of orbitals contributed by the Sb atoms on the pristine surface. This clearly shows that transport through the film can either occur via the mixture of the interface states due to the BC$_3$ contact and pristine surface states of Sb atoms, or from the latter only. By gating the film with a voltage it is possible to selectively choose either mode of transport.

Figure 6 shows the evolution of energy bands for hollow-site contact. The Fermi level tends to be lower in energy for the same sequence of B substitutions, implying that the substrate

**Figure 5.** Spin texture of the three-bilayer Sb (111) film in top-site contact with a single layer of BC$_3$ is shown on the $k_x - k_y$ plane, corresponding to energy of (a) 0.07 eV above the Fermi level and (b) 0.14 eV below the Fermi level.
Figure 6. (a)–(e) Evolution of energy bands of a three-bilayer Sb (111) film in hollow-site contact with B-doped graphene from the concentration of 1/24 to BC₃. Blue (black) circles in (e) indicate contribution from interface (pristine surface) electrons.
contains fewer electrons. In fact, analysis of the Bader charge transfer [18] between the BC\textsubscript{3} layer and the Sb film has indicated that the hollow-site contact has the fewest electrons going into the Sb film, followed by the top-site contact. Listed in table 1, the bridge-site contact induces the largest charge transfer and hence has the strongest binding between the film and the BC\textsubscript{3} layer. The main reason why bridge-site and top-site contacts have larger charge transfers is simply due to the closer contact between atoms in the two configurations.

We present the full band structure of the three-bilayer Sb (111) film in bridge-site contact with BC\textsubscript{3} in figure 7. The size of blue (black) circles indicates the contribution interface (pristine surface) electrons make to the wave function of point \textit{k}. For the Dirac cone near the Fermi level, wave functions corresponding to \textit{k} points close to the $\bar{\Gamma}$ point are largely made of electrons from Sb atoms of the interface layer. At \textit{k} points some distance away from the origin, one band continues to be dominated by the interface electrons, while the other switches to the electrons from the pristine surface. Around 0.25 eV below the Fermi energy, two bands also cross each other at the $\bar{\Gamma}$ point. Both bands are heavily made of electrons from the Sb atoms of the pristine surface. The total density of states of the system is drawn in figure 8(a). Decomposed into individual atoms, local density of states (LDOS) of boron atoms in figure 8(b) indicate that they contribute negligibly to the valence bands of the whole structure, independent of whether they are closer to (black curve) or farther away from (red curve) the surface Sb atoms. Figure 8(c) shows the contributions from an Sb atom in close contact (red curve) with a
boron atom and an Sb in the pristine surface layer. They provide interface and surface states to the valence bands just as figure 7 has explained.

Three energy values are chosen for the analysis of spin-dependent transport of the three-bilayer Sb film in bridge-site contact with BC₃. At 0.1 eV above the Fermi level (figure 9(a)) two equi-energy circles of opposite helix are obtained on the $k_x - k_y$ plane, each having spin direction locked perpendicularly to the momentum. At 0.02 eV, which is exactly the energy level of the Dirac point (figure 9(b)), only one circle is obtained. With only one mode of transport, the current along the $\Gamma - \bar{M}$ direction is 100% spin-polarized with no possibility of back scattering, and the conductance of one quantum unit ($e^2/h$) is only half that of the two-mode cases. If the energy is again shifted downward to, say, 0.008 eV above the Fermi level (figure 9(c)), another two-mode transport appears with complete spin polarization. It is thus possible to switch back and forth between a completely spin-polarized and unpolarized transport by gating the film with continuously adjustable voltage.

We also investigated the dependence of topological conduction on the thickness of Sb film by increasing the number of bilayers from four to six. Their band structures along the $\Gamma - \bar{M}$ direction are drawn in figures 10(a)–(c) for top-site contact of BC₃ respectively. It is clear that

Figure 8. (a) Total density of states derived from figure 7. (b) LDOS of B atoms B1 and B3, with the latter being a nearest neighbor of an Sb atom. (c) LDOS of Sb atoms Sb1 and Sb24. Sb1 is in the pristine surface layer, while Sb24 is a nearest neighbor of B3.
Dirac cones and topological conduction are also present with thicker structures, with the upper cone more related to interface states and the lower one to surface states of the pristine face. There is therefore certain flexibility in synthesizing Sb films for the purpose of topological conduction.

As a final note, we mention briefly the calculation of three-bilayer Sb (111) film deposited on a single layer of BN. Binding energy is almost as weak as that of graphene, and charge transfer is significantly smaller, as listed in table 1. No Dirac cones are formed as a result of this contact.

Figure 9. Spin texture of the three-bilayer Sb (111) film in bridge-site contact with a single layer of BC$_3$ is shown on the $k_x-k_y$ plane, corresponding to energy of (a) 0.1 eV (b) 0.02 eV and (c) 0.008 eV above the Fermi level. There is only one mode of transport in (b).

Dirac cones and topological conduction are also present with thicker structures, with the upper cone more related to interface states and the lower one to surface states of the pristine face. There is therefore certain flexibility in synthesizing Sb films for the purpose of topological conduction.
4. Conclusion

In summary, our calculations have found that an Sb (111) film as thin as three-bilayer can have topological conduction if the film is in contact with a layer of various heterogeneous atoms, including Bi, pure and B-doped graphene. In particular, if the film is in bridge-site contact with BC$_3$, topological conduction can be switched between one-mode and two-mode transport by adjusting gate voltage, with the former being 100% spin-polarized and the latter being either unpolarized or completely polarized. These, together with calculations on thicker films, point to a convenient way to exploit topological transport.

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Figure 10. Energy bands of an Sb (111) film with (a) four bilayers, (b) five bilayers, and (c) six bilayers in top-site contact with a single layer of BC$_3$. Blue (black) circles indicate contribution from interface (pristine surface) electrons.
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