

Formation of a quantum spin Hall state on a Ge(111) surface

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Received 15 September 2015, revised 19 December 2015

Accepted for publication 5 January 2016


Published 29 January 2016



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Abstract

Using first-principles density functional theory (DFT) hybrid functional calculations, we demonstrate the formation of a quantum spin Hall (QSH) state on a Ge(111) surface. We show that a 1/3 monolayer (ML) Cl-covered Ge(111) surface offers an ideal template for metal, such as Bi, deposition into a stable hexagonal overlayer 2D lattice, which we refer to as Bi@Cl-Ge(111). The band structure and band topology of Bi@Cl-Ge(111) are analyzed with respect to the effect of spin-orbit coupling (SOC). The Bi@Cl-Ge(111) exhibits a QSH state with a band gap of 0.54 eV. In contrast, the Au@Cl-Ge(111) is found to be a trivial semiconducting surface. The Ge(111) substrate acts as an orbital filter to critically select the orbital composition around the Fermi level. Our findings offer another possible system for experimental exploration of the growth of 2D topological materials on conventional semiconductor substrates, where the 2D overlayer is atomically bonded to, but electronically decoupled from, the underlying substrate, exhibiting an isolated topological quantum state inside the substrate band gap.

 Online supplementary data available from stacks.iop.org/NANO/27/095703/mmedia

Keywords: 2D topological materials, quantum spin Hall state, spin-orbit coupling, germanium

(Some figures may appear in colour only in the online journal)

1. Introduction

In the last decade, 2D materials have received much attention. Among them, 2D materials that exhibit exotic electronic properties, i.e. the 2D Dirac [1] and topological materials [2], are of particular scientific interest and offer an exciting new realm of electronic devices in the future. Usually, 2D electronic materials are considered in a free-standing form [1–7] to support their exotic electronic properties, which are inherent to the 2D geometry. Recently, however, it has been theoretically proposed that 2D materials can also effectively form on a substrate [8]. In particular, both 2D Dirac states similar to graphene [9] and different forms of 2D topological states [8–12] are shown to form on Si and SiC surfaces. This

is achieved by growing a 2D overlayer structure on the surface of a semiconductor substrate, where the overlayer is atomically bonded to, but electronically decoupled from, the underlying substrate [8], exhibiting an exotic electronic state inside the substrate band gap. Another interesting property of such substrate-supported 2D materials is that the 2D overlayer itself, in the free-standing form, may not be stable (or existing) or have exotic electronic states (such as nontrivial band topology); it is the substrate that on the one hand stabilizes the overlayer and on the other hand generates the exotic electronic states by acting as an orbital filter to critically select the orbital composition around the Fermi level.

There are potentially some very desirable advantages of making directly substrate-supported 2D materials over free-

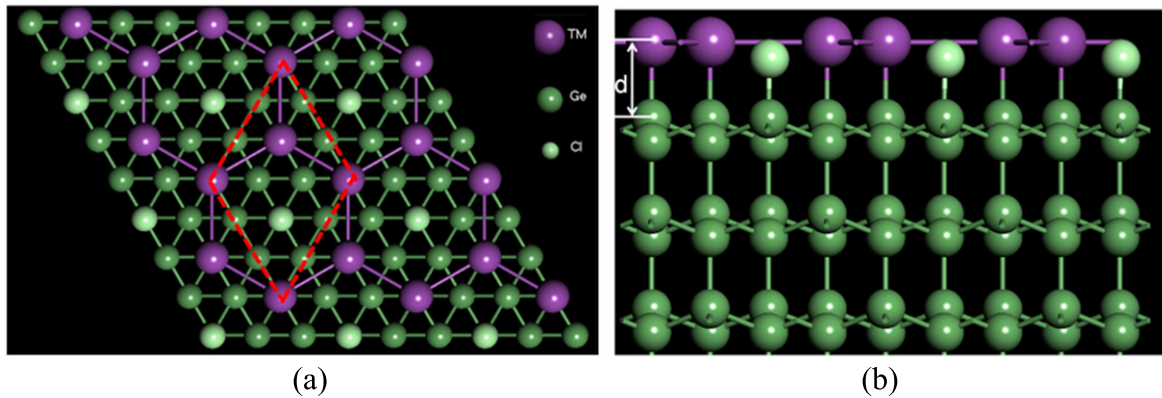


Figure 1. Structure of the Bi (Au) overlayer deposited on the Ge(111)-Cl surface. (a) Top view. Dashed lines indicated surface unit cell. (b) Side view.

standing 2D materials. First, with the help of a substrate, the 2D structures become chemically and mechanically more stable than free-standing 2D materials. Second, the free-standing 2D layers often need to be transferred to a substrate for measurement or for making a device, but their electronic structure and topological properties may change upon being placed on a foreign substrate [13, 14]. Third, devices can be easier to make without the transfer process. However, although the above-mentioned theoretical proposal represents a very interesting idea, it remains to be experimentally confirmed. In this regard, it is important to test whether the idea can be extended to as many different semiconductor substrates as possible. One potential factor that may complicate experiments is surface reconstruction, which is common to semiconductor surfaces. For example, the ground state of the Si(111) surface has a well known and possibly the most complex (7×7) reconstruction [15, 16], as opposed to the bulk termination of a (1×1) surface as assumed in the previous studies [8–11]. These considerations have motivated us to search for new substrates, such as Ge(111), which has a much simpler reconstruction and its bulk termination can be more easily attained [15], to support a Bi layer. On the other hand, we have chosen Bi and Au as metal elements to facilitate a more direct comparison with cases of Si substrates. The choice of Bi is quite popular because it is among the largest SOC elements (elemental SOC gap ~ 1.25 eV) and Bi bi-layer film as well as a number of Bi-containing compounds have been found to be topological insulators (TIs) [17]. Au was chosen because it also has a quite large SOC [18], but a very different valence orbital (one s orbital) composition from Bi (three p orbitals) so that the physical mechanism underlying the formation of overlayer topological states can be revealed by comparison [9–12].

A $1/3$ monolayer (ML) Cl-covered Ge(111) surface exhibits a trigonal symmetry due to strong steric repulsion between the halogen atoms, as observed in experiments [19, 20]. Cl forms a monovalent bond with the Ge(111) dangling bond along the (111) surface normal when Ge is etched in HCl. This chlorine termination inhibits oxide formation and maintains a well ordered surface and is found to

be more stable in air than the putative hydrogen termination achieved by aqueous HF treatment [21–23].

We have calculated the band structure and band topology of Bi on a $1/3$ ML Cl-covered Ge(111) surface [Bi@Cl-Ge(111)]. The Bi overlayer forms a hexagonal lattice, which is both thermodynamically and kinetically stable. The Bi@Cl-Ge(111) surface exhibits a QSH state, qualitatively the same as the Bi@Cl-Si(111) surface albeit with a smaller bulk gap of 0.54 eV. Through comparison with the Au@Cl-Ge(111) surface, which is shown to be a trivial ‘insulator’, the underlying mechanism is revealed, which confirms the previous findings on Si and SiC substrates [9–12].

2. Methods

Because the standard DFT is known to underestimate band gap, in particular producing no gap for bulk Ge, we used a hybrid functional, Heyd–Scuseria–Ernzerhof (HSE) [24], as implemented in the Vienna Ab-initio Simulation Package (VASP) [25], in addition to the more standard DFT method. A slab of six atomic layers of Ge and a $\sqrt{3} \times \sqrt{3}$ surface unit cell were simulated. A vacuum layer of 20 \AA was included in the surface normal direction to avoid interaction between neighboring slabs. The top surface is covered by $1/3$ ML Cl and $2/3$ ML metal atoms (Bi and Au) on a Ge(111) surface, as shown in figure 1. The dangling bonds of Ge atoms in the bottom surface layer are passivated by H. The kinetic energy cutoff was set at 400 eV. Following the Monkhorst–Pack Scheme, Brillouin zone integration was carried out with a $9 \times 9 \times 1$ K point mesh. The symmetry unrestricted optimization for geometry was performed using the conjugate gradient scheme until the maximum atomic forces were smaller than 0.02 eV \AA^{-1} . The self-consistency criteria for electronic structure calculations, with or without SOC, was set at 10^{-6} eV .

3. Results and discussion

We first optimized the proposed 2D overlayer structure. The calculated adsorption length is 2.72 \AA and 2.37 \AA for Bi@Cl-

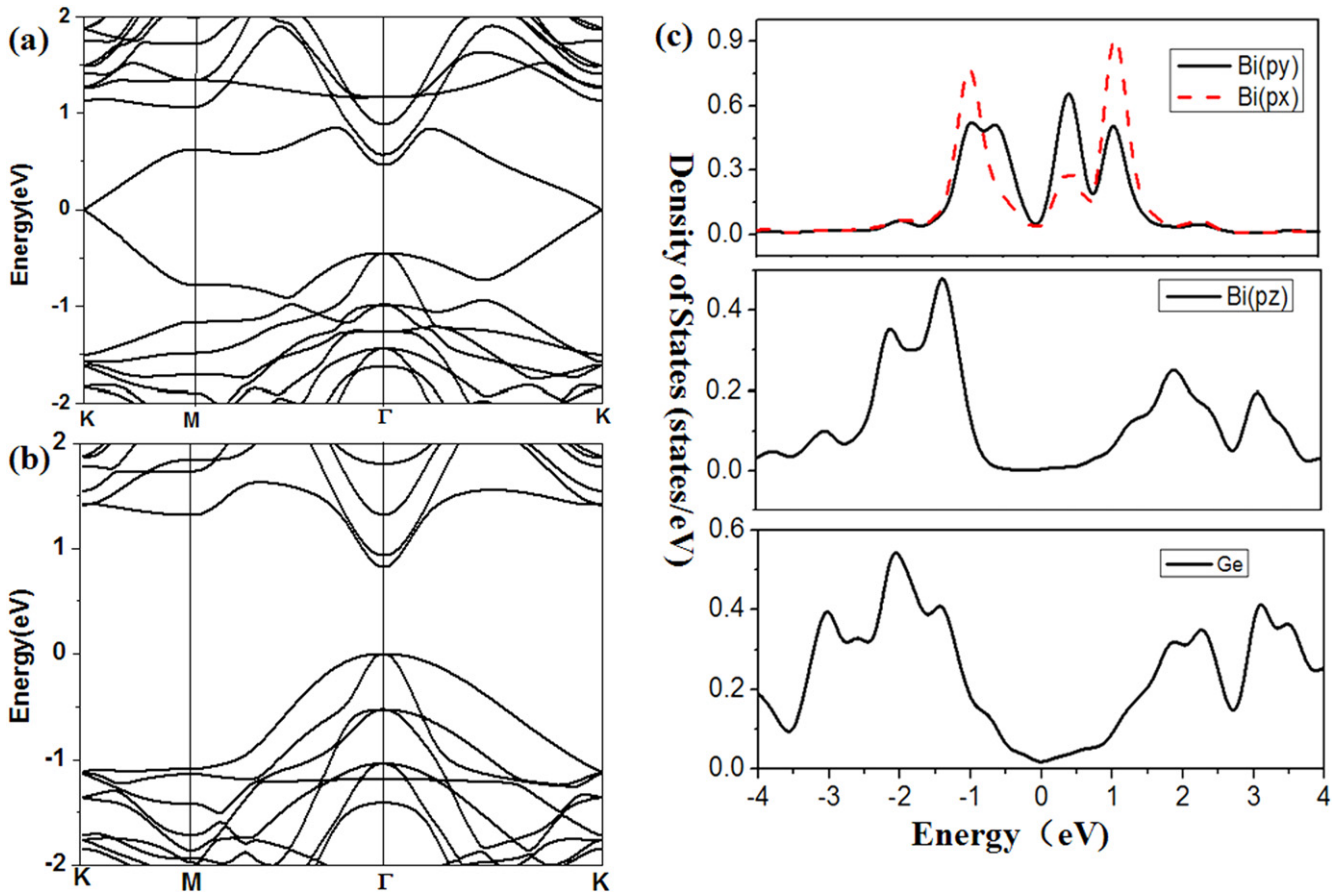


Figure 2. (a) Band structure of Bi@Ge(111) without SOC. (b) Band structure of Au@Ge(111) without SOC. (c) The partial DOS projected onto p_x , p_y , and p_z orbital of Bi, and the total DOS of the nearest neighboring Ge atom.

Ge(111) and Au@Cl-Ge(111), respectively. The adsorption energy is defined as $E_{ad} = [E_{M@Cl-Ge(111)} - (2E_M + E_{Cl-Ge(111)})]/2$. $E_{M@Cl-Ge(111)}$ denotes the energy of metal @ Cl-Ge(111) surfaces, E_M denotes the energy of a single metal atom in the bulk, and $E_{Cl-Ge(111)}$ denotes the energy of the Cl-Ge(111) surface without metal. The adsorption energies are calculated to be 2.65 eV and 2.36 eV for Bi and Au, respectively. The adsorption energy of Bi@Cl-Ge(111) is slightly smaller than that of Bi@Cl-Si(111) (2.99 eV) [8], while the adsorption length of Bi@Cl-Ge(111) is slightly larger than that of Bi@Cl-Si(111) (2.46 Å) [8]. Nevertheless, these data also indicate a very strong binding between the deposited metal atoms and the exposed surface Ge atoms in the Ge(111) surface. Thus, a high stability of the proposed 2D overlayer lattice is also expected.

Next, the band structures of the optimized Bi(Au)@Cl-Ge(111) surfaces were calculated, as shown in figures 2(a) and (b) without SOC and in figures 3(a) and (b) with SOC. Also shown in figure 2(c) are the corresponding partial densities of states (DOS) projected onto the p_x , p_y , and p_z orbitals of Bi, and the total DOS projected onto the nearest neighboring Ge atom of Bi. From figure 2(a), we see that the bulk band gap at point Γ is about 0.91 eV. It is slightly larger than the experimental value (0.8 eV) because of the quantum confinement in the thickness direction of the thin slab we

used. Consistently, the bulk band gap is calculated to be about 0.15 eV (instead of zero) using the standard DFT method (see figure 4(a) below). There are two Dirac bands residing inside the bulk gap of Ge and a Dirac point at K point, and the Fermi level is located exactly at the Dirac point. Figure 2(b) shows the band structure of the Au@Cl-Ge(111) surface without SOC. In sharp contrast to Bi@Cl-Ge(111), the band structure of Au@Cl-Ge(111) is very different. It is a typical semiconductor surface with a band gap of 0.83 eV. There is no Dirac band.

From the top panel of figure 2(c), we see that the Dirac bands mainly consist of p_x and p_y orbitals of Bi, with little contribution from the p_z orbital of Bi (middle panel) and Ge orbitals (bottom panel). Also from the bottom two panels of figure 2(c), we see that there is a strong overlap between the p_z orbital of Bi and orbitals of neighboring Ge atoms, indicating that the p_z orbital of Bi hybridizes strongly with the sp^3 dangling bond of the exposed surface Ge atom. This observation confirms an interesting substrate orbital-filtering mechanism, proposed previously on Bi@Cl-Si(111), that the Ge substrate (in place of Si substrate) selectively removes the p_z orbital of Bi, so that only the p_x and p_y orbitals of Bi are left at the Fermi level. This mechanism is the key to producing the surface QSH state, as we discuss further below.

The band structures with SOC are shown in figure 3. Comparing the band structures with (figure 3(a)) and without

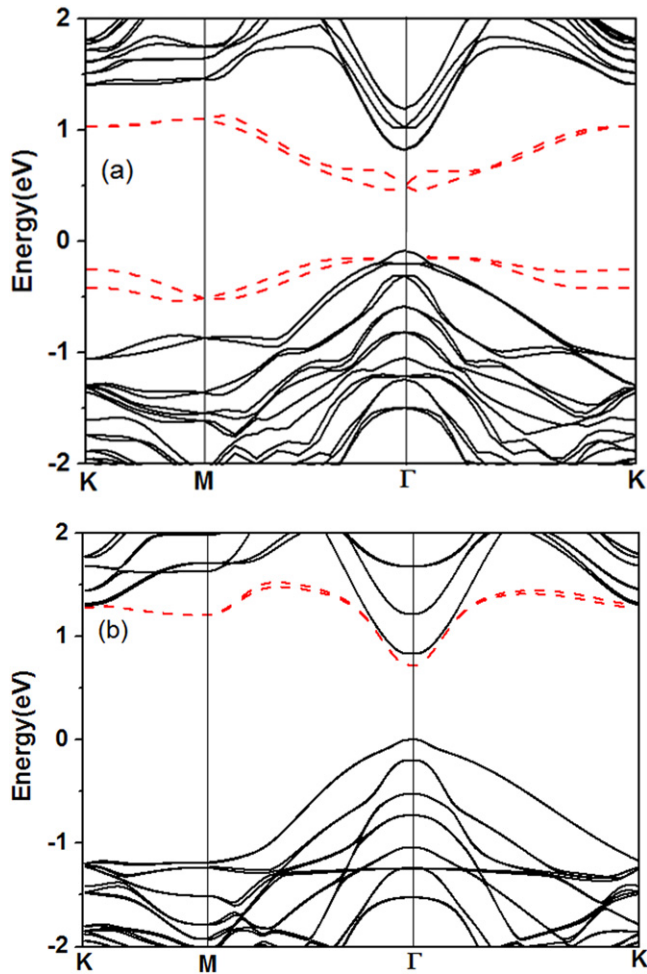


Figure 3. (a) Band structure of Bi@Ge(111) with SOC. (b) Band structure of Au@Ge(111) with SOC. The red dashed lines indicate Bi (or Au) bands.

SOC (figure 2(a)) for Bi@Cl-Ge(111), one sees that two Dirac bands split by SOC, but remain mostly inside the bulk gap of Ge. The SOC gap at the K point is ~ 1.28 eV, while the global SOC gap is ~ 0.54 eV near the Γ point between the upper Dirac band and the top of the Ge valence band. Compared with the band structures of Bi@Cl-Si(111), here the two Dirac bands split further apart [8]. For heavy atoms adsorbed on the Si(111) surface, it has been shown that their band structures can be captured by a simplified four-band model [8, 11]. In this model, one interesting outcome is that the SOC gap does not increase monotonically with the increasing strength of SOC [11], as in the two-band model of graphene [2]. Specifically, SOC opens an energy gap between the upper and lower Dirac bands at the K point as well as two energy gaps between the Dirac bands and two flat bands at the Γ point, which are all topologically nontrivial. With the increasing SOC, all the gaps increase, leading to two regimes of different behavior. At small SOC, the global gap is at the K point, which increases with the increasing SOC; but at large SOC beyond a ‘critical’ SOC, the global gap shifts to the Γ point, which decreases with increasing SOC [11]. The electronic structure of Bi@Cl-Ge(111) belongs to the large SOC

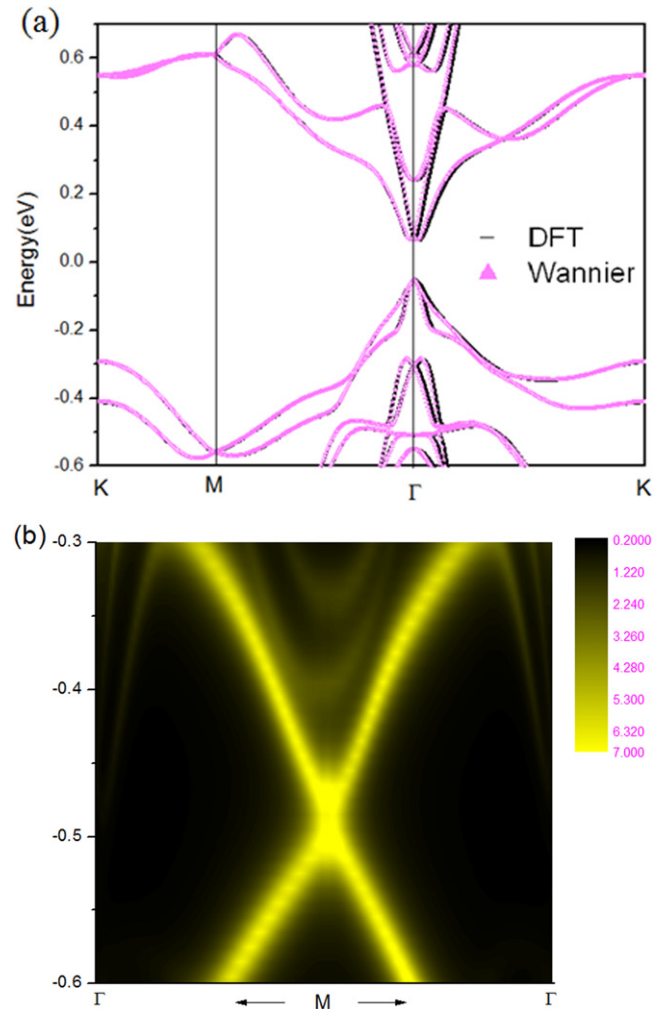


Figure 4. (a) Comparison of band structures for Bi@Cl-Ge(111) calculated by DFT (black lines) and Wannier function method (pink triangles). (b) The Dirac edge states for Bi@Cl-Ge(111) within the SOC-induced band gap. Scale bar is indicated on the right.

regime as described by the four-band model. This suggests that Bi@Cl-Ge(111) is a promising 2D TI material for practical applications in electronics and spintronics. But for Au@Cl-Ge(111), comparing figure 2(b) with figure 3(b), the SOC causes little change in band structure, except for a small change of energy gap at point Γ (0.83 eV without SOC, 0.72 with SOC) and some Rashba-type spin splitting.

It is well known that the SOC-induced gap opening at the Dirac point indicates the possible existence of a 2D TI state. Specifically in the present case, the substrate orbital-filtering effect removes the Bi p_z orbital and leaves behind only p_x and p_y orbitals at the Fermi level, so that the system may produce 2D TI states according to a four-band model of topological phase in a hexagonal lattice [26]. To check this, we calculated the topological edge state by the Wannier90 package [27], as shown in figure 4, and the Z_2 topology number for Bi@Cl-Ge(111). Figure 4(a) shows the fitting of tight-binding band structure around the Fermi level using the Wannier90 package to the standard DFT band structure, which is in a very good agreement. Figure 4(b) shows the calculated edge states that

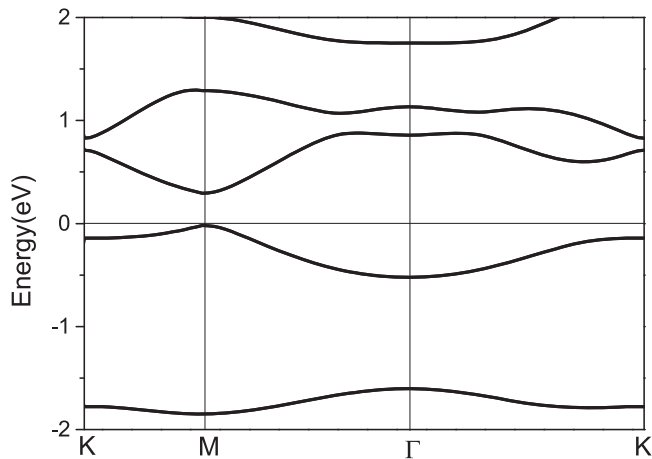


Figure 5. The band structure of the free-standing planar hexagonal lattice of Bi.

connect the top of the valence band and the bottom of the conduction band of the bulk gap, forming a 1D Dirac cone at point *M*. As the spatial inversion symmetry is broken in the system, the Z_2 topology number is calculated by considering the Berry gauge potential and Berry curvature associated with the Bloch wave functions [27, 28], which does not require any specific point-group symmetry. The calculated topology number is $Z_2 = 1$ for Bi@Cl-Ge(111). We also confirmed this by using Wilson loop methods [29] based on the $U(2N)$ non-Abelian Berry connection. Thus, both the 1D topological edge state and nontrivial topological number indicate that the Bi@Cl-Ge(111) is a 2D TI with a large gap of 0.54 eV.

To illustrate the critical role of the substrate, we have calculated the energy band structure of the free-standing planar hexagonal lattice of the Bi layer (shown in figure 5). It is found that the free-standing planar structure is a topologically trivial insulator ($Z_2 = 0$), but becomes topologically nontrivial when being deposited on Ge(111) substrate. This result highlights the importance of the orbital-filtering effect imposed by the substrate, in agreement with [8].

4. Conclusion

We have calculated the band structure, overlayer edge state and Z_2 topological number of a Bi(Au)@Cl-Ge(111) surface, using HSE and Wannier function methods. Our calculations show that the Bi@Cl-Ge(111) exhibits a 2D TI state with the global gap 0.54 eV. The Cl-Ge(111) substrate selectively removes the p_z orbital of Bi away from the Fermi level, leaving the p_x and p_y orbitals to form two Dirac bands that are topologically nontrivial. On the contrary, the band structure of Au@Cl-Ge(111) is a normal semiconductor surface with a band gap of 0.72 eV. Our findings provide another potential material system for future experimental research in searching for topological quantum phases on conventional semiconductor surfaces.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No.11304121), the Natural Science Foundation of Shandong Province (Grant No. ZR2013A1004), and the doctoral foundation of the University of Jinan (Grant No. XBS1402). MZ and FL acknowledge support from DOE-BES (Grant # DE-FG02-04ER46148). We thank NERSC and the CHPC at the University of Utah for providing the computing resources.

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