Stable Nontrivial Z_2 Topology in Ultrathin Bi (111) Films: A First-Principles Study

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Recently, there have been intense efforts in searching for new topological insulator materials. Based on first-principles calculations, we find that all the ultrathin Bi (111) films are characterized by a nontrivial Z_2 number independent of the film thickness, without the odd-even oscillation of topological triviality as commonly perceived. The stable nontrivial Z_2 topology is retained by the concurrent band gap inversions at multiple time-reversal-invariant k points with the increasing film thickness and associated with the intermediate interbilayer coupling of the Bi film. Our calculations further indicate that the presence of metallic surface states in thick Bi (111) films can be effectively removed by surface adsorption.

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As a new insulating phase in condensed matter, the topological insulator (TI) has recently attracted a great deal of attention [1]. The TI is distinguished from the conventional insulator by its unique gapless surface states residing in the middle of a band gap as a consequence of the so-called Z_2 topology encoded in the wave functions. There has been an intensive search for TI materials. Although quite a few compounds have been found to be 3D TIs [2–6], up to now only the HgTe quantum well is verified to be a 2D TI (or a quantum spin Hall insulator) experimentally [7]. Recently, Murakami predicted a single bilayer (BL) Bi (111) film to be an elemental 2D TI [8,9] and further speculated the multi-BL Bi (111) film to exhibit an odd-even oscillation of topological triviality with film thickness [8] by considering the multi-BL film as a stack of BLs with no or very weak inter-BL coupling [10]. Generally speaking, the 2D TI phase in thin films is commonly perceived to depend sensitively on film thickness, as shown for the Bi_2Se_3 and Bi_2Te_3 ultrathin films [11]. The requirement of fine-tuning the thickness makes the experimental fabrication of 2D TIs rather difficult. Therefore, it is desirable to search for new materials or new schemes to obtain a 2D TI.

In this Letter, based on the first-principles calculations of band structures and wave function parities, we find that in fact all the Bi (111) ultrathin films are characterized by a nontrivial Z_2 number independent of the film thickness. The films with 1–4 BLs are intrinsic 2D TIs, while those with 5–8 BLs are 2D TIs sandwiched with trivial metallic surfaces that can be extrinsically removed by surface adsorption. This finding is in direct contrast to the odd-even oscillation of topological triviality speculated for the Bi films [8], as well as to the thickness-dependent topology shown for other 2D films [11]. The surprisingly stable 2D TI phase in the Bi(111) films is found to be retained by a concurrent band gap inversion at multiple time-reversal-invariant k points when the film thickness is increased. A detailed analysis of the 2- and 3-BL Bi films indicates that the intermediate inter-BL coupling plays an important role in defining their unique topological property.

Bismuth is one of the main group elements that has the strongest spin-orbit coupling, a fundamental mechanism to induce the Z_2 topology. For this reason, many 3D TIs make use of Bi, even though 3D bulk Bi itself is topologically trivial [2]. The electronic properties of Bi, such as the bulk band structure [12], the surface states [13], and the semimetal-to-semiconductor transition [14,15], have been well established in the literature. The outermost shell of Bi has the electron configuration $6s^2 6p^3$. It tends to form three bonds to close the shell. The single-crystal Bi has a bilayered structure, with an ABC stacking sequence along the (111) direction [Fig. 1(a)]. Within each BL, every Bi atom forms three σ bonds with its nearest neighbors in a trigonal pyramidal geometry. Projecting onto the (111) plane, the BL forms a hexagonal lattice with two atoms per unit cell [Fig. 1(b)]. There are three key structural parameters to define the lattice: the in-plane lattice constant a, the intra-BL bond angle α (or the BL height d_1), and the inter-BL spacing d_2. Our calculated bulk structural parameters as shown in Figs. 1(a) and 1(b) agree well with previous calculations [13]. The Bi (111) ultrathin films, consisting of a few number of stacked BLs, have slightly relaxed structural parameters relative to the bulk values. Specifically, α approaches 90° and d_2 increases by about 6%. This implies a slightly enhanced p-orbital feature of the intra-BL bonds and a weakening of the inter-BL coupling.

To identify the 2D TI phase, a single Z_2 topological number (ν) is used as the ''order parameter'' [10]: $\nu = 1$

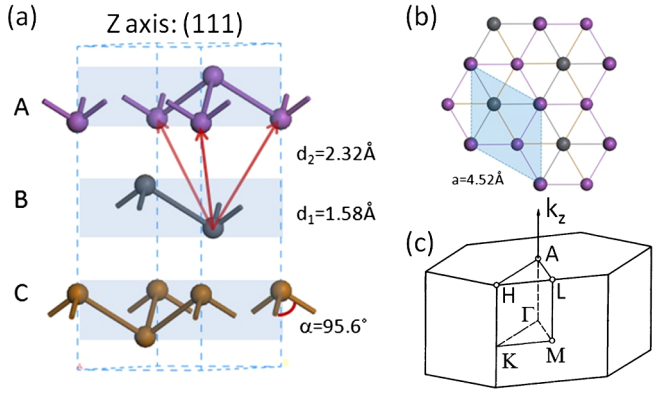

FIG. 1 (color online). (a) The hexagonal unit cell of single-crystal bismuth. (b) The top view of the Bi lattice. (c) The first Brillouin zone of the hexagonal lattice.

indicates a topologically nontrivial phase; $\nu = 0$ indicates a trivial phase. The calculation of the Z_2 number can be dramatically simplified by the so-called "parity method" [2], if the system is space inversion invariant, as in the case of the Bi (111) film. Accordingly, the Z_2 number of Bi films can be obtained from the wave function parities at four time-reversal-invariant k points (K_i), one Γ, and three M's, as

$$\delta(K_i) = \prod_{m=1}^{N} \xi_{2m}^{i}, \qquad (-1)^{\nu} = \prod_{i=1}^{4} \delta(K_i) = \delta(\Gamma)\delta(M)^3,$$

where $\xi = \pm$ is the parity eigenvalues and N is the number of the occupied bands.

Single-electron wave function parities are calculated within the density functional theory using the plane wave basis, as implemented in the ABINIT package [16]. We employ the local density approximation [17] and the Hartwigsen-Goedecker-Hutter pseudopotential [18], which is generated on the basis of a fully relativistic all-electron calculation and tested to be accurate for heavy elements like Bi. The spin-orbit coupling is included in the self-consistent calculations as described in Ref. [19]. To model the thin film, a supercell of slab is used with periodic boundary conditions in all three dimensions with a 10 Å thick vacuum layer in the (111) direction to eliminate the interslab interaction. A plane wave cutoff of 24 Ry and a Γ-centered k-point mesh of $10 \times 10 \times 1$ are used. All the atomic positions are fully relaxed for each film.

Table I shows the calculated Z_2 numbers for 1- to 8-BL films. Surprisingly, all the films we calculated are characterized by the nontrivial Z_2 number ($\nu = 1$), in direct contrast to the oscillation of topological triviality as commonly perceived. We notice that the parity $\delta(\Gamma)$ and $\delta(M)$ simultaneously change their signs for every 2 BLs. This kind of parity oscillation, which originates from the inverted band gap of a 3D TI, has been reported in Bi_2Se_3 and Bi_2Te_3 ultrathin films but only at the Γ point [11]. The uniqueness of Bi film is the inverted band gaps at both the Γ and M points due to the strong spin-orbit coupling of

TABLE I. The total parity at the Γ and M points and the Z_2 number of Bi (111) films with different thickness.

No. of BLs	1	2	3	4	5	6	7	8
$\delta(\Gamma)$	+	+	−	−	+	+	−	−
$3\delta(M)$	−	−	+	+	−	−	+	+
ν	1	1	1	1	1	1	1	1

Bi [2]. As a consequence, the parity oscillation under the quantum confinement occurs concurrently at all time-reversal-invariant k points (one Γ and three M's) as the film thickness increases. Being the product of $\delta(\Gamma)$ and $\delta(M)$, the Z_2 number shows up as the "beat" of two oscillations, which makes the 2D TI phase in Bi ultrathin films much more stable than in the Bi_2Se_3 and Bi_2Te_3 films. We expect that the Z_2 number of Bi films will eventually change at some point when the phase difference between the oscillations at Γ and M accumulates to π, but this requires calculations of much thicker Bi films possibly beyond the current computational capability.

It has been predicted that the 1-BL Bi (111) film is a 2D TI [8,9]. If we could regard the n-BL film as a stack of these nontrivial 1-BL films with no inter-BL coupling, then all the bands would have n-fold degeneracy and the total Z_2 number of the film is simply $\nu = N \bmod 2$, naturally leading to an odd-even oscillation of Z_2 topology: $\nu = 1$ for the odd-BL stacks and $\nu = 0$ for the even-BL stacks [10,20]. Such an odd-even oscillation of Z_2 topology can be extended to the weak inter-BL coupling regime under the adiabatic approximation, which was speculated to be applicable to the Bi(111) films [8]. However, our first-principles results show that the Bi (111) film may not be adiabatically connected to the zero inter-BL coupling limit.

The Bi (111) film actually represents a special interesting class of films having an intermediate inter-BL coupling strength. The inter-BL bond energy is calculated to be 0.3–0.5 eV per bond, which is noticeably larger than the typical values of weak interfacial bonds, such as van der Waals bond but smaller than the values of typical chemical bonds. This intermediate inter-BL coupling may have a significant influence on the topological property. To reveal the influence, we have calculated a set of "model" Bi films with their inter-BL coupling tuned gradually from the real intermediate regime to the hypothetical weak coupling regime that could be adiabatically connected to the zero coupling limit. This is done by artificially increasing the inter-BL distance from the equilibrium value d_2 with an increment of Δd_2, by using the supercell technique. Here we take 2-BL (3-BL) film as an example of even-BL (odd-BL) films. Figures 2(a) and 2(b) show the evolution of band structures as a function of Δd_2 for the 2-BL and 3-BL films, respectively. For $\Delta d_2 = 0$, the figures show the realistic band structures of the 2-BL and 3-BL films, while for $\Delta d_2 = 4$ Å, the corresponding band dispersion of hypothetical films shows a weak inter-BL

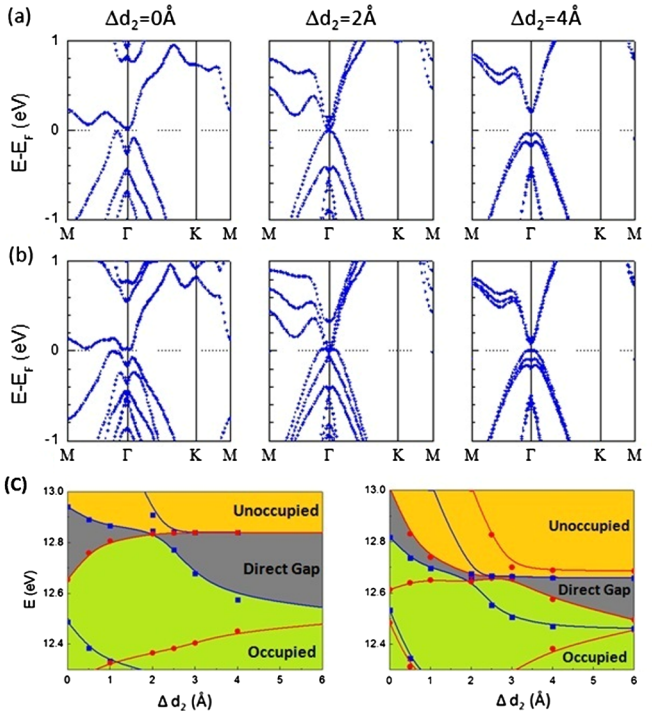

FIG. 2 (color online). The band structure of (a) 2 BLs and (b) 3 BLs under different inter-BL spacing. (c) The energy level at the Γ point of (left) 2 BLs and (right) 3 BLs as a function of the inter-BL spacing. The red (circle) lines indicate even-parity levels. The blue (square) lines indicate odd-parity levels.

coupling case. We note that as the Δd_2 is tuned from 4 to 0 Å, the direct gap at Γ point undergoes a closing and reopening process, indicating that the realistic band dispersion of Bi films may not be adiabatically connected to the zero coupling limit.

To trace the change of topology with the inter-BL coupling, we analyze the parity property of the energy levels at Γ point as a function of Δd_2 in Fig. 2(c) for the 2-BL (left) and 3-BL (right) Bi films, respectively. When Δd_2 is reduced, the n-fold degeneracy for the zero coupling limit is lifted by the inter-BL coupling. Although the variation of band gaps is similar for the 2-BL and 3-BL films, the change of total parity of all the occupied bands shows quite different behaviors. For the 2-BL film, each doubly degenerate level is split into one odd-parity sublevel with higher energy and one even-parity sublevel with lower energy. Consequently, the lowest unoccupied level has the even parity [red, left panel of Fig. 2(c)], while the highest occupied level has the odd parity [blue, left panel of Fig. 2(c)]. As Δd_2 is reduced, a level crossing and hence a parity exchange happen at $\Delta d_2 = 2$ Å due to the opposite parities of the two crossing levels, leading to a change of ν from 0 (for the noncoupling even-BL films) to 1 and hence converting the Z_2 number of the 2-BL film from trivial to nontrivial. The situation, however, is different for the 3-BL film. Now, each threefold degenerate level is split into three sublevels, always with one odd-parity sublevel sandwiched by two even-parity sublevels (right panel of Fig. 2). Consequently, both the lowest unoccupied and highest occupied levels have the same even parity. As Δd_2 is reduced, a level anticrossing instead of crossing happens and the number of odd- and even-parity sublevels for both the occupied and unoccupied bands remains unchanged, resulting in no change to the nontrivial Z_2 topology of the 3-BL film. We have also did model calculations of 3-BL film by separating 1 BL away from 2 BLs, which indicates the same physical picture [20].

In the above simple picture, we have implicitly used the prerequisite condition that, with the changing inter-BL coupling, the level crossing or anticrossing happens only at the Γ point but not at the M point and involves only a few levels close to the band gap, which can be satisfied only by an inter-BL coupling that is not too strong. Also, the coupling cannot be too weak in order to move away from the weak coupling regime that is adiabatically connected to the zero coupling limit. Therefore, the intermediate coupling strength is a mandatory condition for the nontrivial Z_2 topology. Such an ''intermediate coupling principle'' may be utilized in the search for the 2D TI phase in other materials.

In Fig. 3(a), we plot both the direct and indirect band gaps as a function of the film thickness. Within the calculated film thickness range, the direct gap always remains open, which is essential for a well-defined Z_2 number. Below 4 BLs, the film is a semiconductor having a nontrivial Z_2 number and hence representing an intrinsic 2D TI. However, the indirect band gap becomes negative above 4 BLs, leading to a semiconductor-semimetal transition [15]. The semimetallization arises from two overlapping bands around the Fermi level, as shown in Fig. 3(b) for the 5-BL film as an example. It has been pointed out [13,15] that these two bands have evident surface band features and tend to become gapless at the Γ and M points in the limit of a semi-infinite system. From this view, the films from 5 to 8 BLs can be regarded as a 2D TI sandwiched between two trivial metallic surfaces [top panel, Fig. 3(c)]. The meaning of ''trivial'' here is twofold. On the one hand, if we consider the surface as an individual 2D system, its Z_2 number is 0 (trivial), as obtained from the surface band parities at the Γ and M points [see Fig. 3(b)]. Therefore, the surface bands have no contribution to the nontrivial Z_2 number of the film. On the other hand, in the limit of a semi-infinite system, because bulk Bi is a 3D Z_2 topologically trivial insulator, these trivial metallic surface bands are not robust as those of a 3D strong TI and hence, in principle, can be easily removed by surface defects or impurities, e.g., via surface adsorption. To test this idea, we have terminated the two surfaces with H atoms as schematically depicted in the bottom panel of Fig. 3(c) and repeated the calculation. We find that, upon surface adsorption, the two surface bands are separated apart, opening a gap around the Fermi level, as shown in

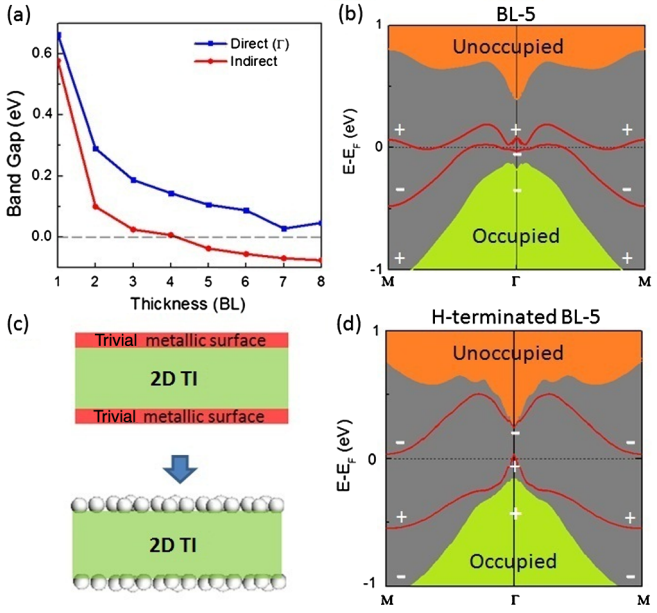

FIG. 3 (color online). (a) The direct (Γ point) and indirect band gap as a function of the film thickness. (b) The band structure and the parity information of 5 BLs. (c) A schematic depiction of the electronic property of a Bi (111) film before and after the H termination. (d) The band structure and the parity information of H-terminated 5 BLs.

Fig. 3(d). Meanwhile, the H atoms introduce additional occupied bulk bands, which are found to be topologically trivial, so that the Z_2 number remains nontrivial [see Fig. 3(d)]. Thus, by the extrinsic effects of H surface adsorption, the thicker films above 5 BLs are effectively converted into 2D TIs similar to those ultrathin films below 4 BLs. We note that because the local density approximation is known to underestimate the band gap, the actual transition thickness is likely to be thicker than the 4-to-5 BLs, but the overall trend of behavior we show here should remain valid.

In summary, the film below 4 BLs is an intrinsic 2D TI with the band structure consisting of ''molecular orbital'' levels without distinction of surface bands from bulk bands, as shown in Figs. 2(a) (left panel) and 2(b) (left panel) for the 2-BL and 3-BL film, respectively. Above 4 BLs, the band structure is made of surface bands superimposed onto a 2D projected bulk band, as shown in Fig. 3(a) for the 5-BL film. The projected 2D bulk bands still keep the nontrivial topology of a 2D TI with a sizable gap, but the surface bands gradually appear in the middle of the projected bulk band gap with the increasing film thickness (see also [15]), leading to a semiconductor (1–4 BLs) to a semimetal (5–8 BLs) transition. The trivial metallic surface states can be removed by surface H adsorption [Fig. 3(d)], which effectively converts the Bi films into true 2D TIs.

Our finding of all the ultrathin Bi (111) films being 2D TIs independent of thickness may provide a possible explanation of the recent observation of 1D topological metal on the Bi (114) surface [21] and will stimulate more experimental interest in this intriguing system. The Bi (111) films above 6 BLs have already been successfully grown via molecular beam epitaxy [22], and hopefully even thinner Bi films can be grown in the near future. It should be noted that the substrate may have additional effects on the electronic structure and hence the topological properties of Bi films, which are of interest for future studies. The physical mechanism we identified for retaining the stable nontrivial Z_2 topology has broad implications. Most importantly, tuning the interlayer coupling to the intermediate regime, so as to remove the odd-even oscillation of topological triviality, can be applied as a general strategy to obtain the TI phase.

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