Crystal Field Effect Induced Topological Crystalline Insulators In Monolayer IV-VI Semiconductors

Junwei Liu,1 Xiaofeng Qian2, and Liang Fu1

1Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139; 2Department of Materials Science and Engineering, Dwight Look College of Engineering, Texas A&M University, College Station, TX 77843.

Two-dimensional (2D) topological crystalline insulators (TCIs) were recently predicted in thin films of the SnTe class of IV-VI semiconductors, which can host metallic edge states protected by mirror symmetry. As thickness decreases, quantum confinement effect will increase and surpass the inverted gap below a critical thickness, turning TCIs into normal insulators. Surprisingly, based on first-principles calculations, here we demonstrate that (001) monolayers of rocksalt IV-VI semiconductors XY (X= Ge, Sn, Pb and Y=S, Se, Te) are 2D TCIs with the fundamental band gap as large as 260 meV in monolayer PbTe, providing a materials platform for realizing two-dimensional Dirac fermion systems with tunable band gap. This unexpected nontrivial topological phase stems from the strong crystal field effect in the monolayer, which lifts the degeneracy between $p_{x,y}$ and $p_z$ orbitals and leads to band inversion between cation $p_z$ and anion $p_{x,y}$ orbitals. This crystal field effect induced topological phase offers a new strategy to find and design other atomically thin 2D topological materials.

Topological insulators (TIs) have attracted extensive attention owing to their fundamental theoretical interests and potential applications [1–3]. The interplay between crystallography and electronic band topology has further given birth to a new type of topological phases, termed topological crystalline insulators (TCIs) [4, 5]. The first example of TCIs was recently predicted in SnTe class of IV-VI semiconductors [6]. They host even number of Dirac fermions in the monolayer, which lifts the degeneracy between $p_{x,y}$ and $p_z$ orbitals and leads to band inversion between cation $p_z$ and anion $p_{x,y}$ orbitals. This crystal field effect induced topological phase offers a new strategy to find and design other atomically thin 2D topological materials.

RESULTS AND DISCUSSION

The band structure plot displayed in Fig. 1(a) shows that monolayer SnTe is a semiconductor with a small indirect gap located around the X point. Moreover, the nearby W-shape conduction band and M-shape valence band provide a clear sign of band inversion at X point with a large inverted gap (denoted by $E_g^X$) of about $-0.6$ eV at its optimized equilibrium lattice constant of $L_{\text{opt}}=6.2$ Å. Negative sign of $E_g$ indicates an inverted gap. To confirm this band inversion, we performed first-
FIG. 1. (a) Band structure of monolayer SnTe, where the size of red dots indicates the weight of Sn $p_z$ orbital; the inset is the 2D Brillouin zone of (001) thin films; (b) Band gap at X point ($E_g^X$) and fundamental gap ($E_g$) of monolayer SnTe as a function of lattice constant ($L$). As $L$ increases, monolayer SnTe undergoes a topological phase transition from $|N_M|=2$ to $N_M=0$. When $L>6.2$ Å, it is a fully gapped semiconductor; otherwise, it is a semi-metal; The inset is the band structure evolution around the transition point (red: $L=6.4$ Å; blue: $L=6.6$ Å; black: $L=6.8$ Å).

principles calculations of monolayer SnTe under a series of biaxial elastic strain [61][23][42]. As shown in Fig. 1(b), when lattice constant ($L$) increases, $E_g^X$ monotonically enlarges and reaches zero at a critical lattice constant of $L_c = 6.6$ Å. Beyond $L_c$, $E_g^X$ becomes positive, indicating a trivial topological phase. The monotonic change of $E_g^X$ is very similar to those in Bi2Se3-type topological insulator [42], which comes from the different parties of bottom conduction band and top valence band at X points: one corresponds to bonding states and the other corresponds to anti-bonding states, whose energy changes oppositely under the biaxial strain. However, the fundamental gap (denoted by $E_g$) has a different behavior. When $L < 6.2$ Å, $E_g$ is negative, manifesting a semi-metallic nature. As $L$ increases, $E_g$ first increases to a local maximum ($\sim 80$ meV) at $L = 6.4$ Å, and then decreases to zero at $L_c$, forming a Dirac cone at X point as shown in the inset of Fig. 1(b). The above strain-dependent band structure analysis demonstrates that monolayer SnTe without strain has an inverted gap at X point with a negative value. According to the parity criteria [43], it can not be Z2 topological insulator as there are two X points in the whole BZ. However, bulk SnTe has rocksalt crystal structure, and therefore its (001) monolayer thin films possess $z \rightarrow -z$ mirror symmetry which allows us to define the corresponding mirror Chern number $N_m$ [44]. Following the similar analysis and argument [19], we can infer monolayer SnTe is a 2D TCI with non-zero mirror Chern number $|N_m| = 2$.

FIG. 2. Edge states of monolayer SnTe along [001] direction with lattice constant $L = 6.4$ Å (top panel) and the schematic (001) ribbon model (bottom panel). The inset is schematic edge states for the whole Brillouin zone.
states can realize quantized transport. Moreover, the mirror is connected with the spin in the system, and transport current should be also spin-polarized.

We also performed DFT calculations for multi-layer thin films using the experimental lattice constant of bulk SnTe, \( L_{\text{exp}} = 6.312 \text{ Å} \), complementing our previous work \[19\]. Figure 3(a) reveals a non-monotonically change in \( E_g^X \) with increasing thickness. Two critical thickness values divide the phase diagram into three parts. More specifically, except three, five, and seven layers of SnTe thin films, all other thin films have negative (or, inverted) \( E_g^X \). For thin films of more than 17 layers, \( E_g^X \) almost stays constant, reaching the gap of bulk SnTe. As the thickness gradually decreases, the confinement effect increases, driving \( E_g^X \) to decrease and reach zero at about 7 layers. However, the gap didn’t continue its monotonic change for thin films of less than 5 layers. Instead, gap closes again between monolayer and 3 layers due to the aforementioned inverted gap \( E_g^X \) in monolayer SnTe. The thickness-dependent inverted gap is consistent with our previous work \[19\] in the multi-layer case, providing a complete phase diagram shown in Fig. 3(a).

To elucidate the underlying mechanism of band inversions, we analyzed the orbital evolution in detail and the result is presented in Fig. 3(b). Previous works show that the fundamental gap of IV-VI semiconductor is around \( L \) (\( X \)) points for bulk (thin films), and the bands near the Fermi level are mainly composed of \( p \) orbitals of cation and anion (Sn and Te for SnTe) \[6 \[19\]. As shown in Fig. 3(b), we start from the atomic limit where the chemical bonding between different atoms are ignored and focus on the \( p \) orbitals. After taking SOC into account, the six-fold degenerate \( p \) orbitals split into four-fold degenerate \( J = 3/2 \) states and two-fold degenerate \( J = 1/2 \) states. \( J = 3/2 \) states are pushed up while \( J = 1/2 \) states are lowered down in energy as shown in Step (i).

We then included the hopping between those atomic orbitals (chemical bonds). For the bulk states, the \( pp \) hopping between cation and anion vanishes at \( L \) points, and the \( sp \) and \( pd \) hopping will play a vital role and lead to the four-fold degenerate \( J = 3/2 \) states to further split into \( J_z = \pm 3/2 \) and \( J_z = \pm 1/2 \) states (\( z \) along [111] direction). More importantly, the splitting is even strong enough to lower Sn’s \( J = 1/2, J_z = \pm 1/2 \) states than Te’s \( J = 3/2, J_z = \pm 1/2 \) states, driving SnTe into 3D TCI phase (Step (ii)). While for PbTe, the splitting induced by chemical bonding is not large enough to promote the band inversion although SOC is even stronger.

For the thin films, the states around \( X \) points mainly inherit from the bulk states at \( L \) point. When films are thick enough, all the properties of those states such as orbital weights and band orders are preserved, which ensure all the thin films thicker than a critical thickness (7 layers for SnTe) have negative inverted gap at \( X \) points and possess the nontrivial topological phase, i.e. \( |N_{\text{triv}}| = 2 \). However, as the thickness decreases, the confinement effect will increase, hence enlarge the energy gap between anion and cation like in the normal semiconductor, giving rise to vanishing band inversion (see Step (iii) in Fig. 3(b)) and topological phase transition as shown around 7 layers in Fig. 3(a).

So far, all \( p_{x,y,z} \) orbitals are treated equally. This is reasonable for bulk and thick films, since the difference between all \( p_{x,y,z} \) orbitals is negligible. However, it is no longer true for atomically thin 2D materials as the chemical environment (crystal field) for \( p_z \) and \( p_{x,y} \) is completely different, where \( z \) is along [001] direction. For \( p_{x,y} \) orbitals, the crystal field is similar to the bulk where the \( p_{x,y} \) orbitals between anion and cation form both \( \sigma \) and \( \pi \) type bonding. However, \( \sigma \) bond is absent for the \( p_z \) orbitals in monolayer. Such kind of asymmetric crystal field leads to the on-site energy of \( p_z \) higher or lower than \( p_{x,y} \) for cation (Sn) or anion (Te), respectively, i.e. \( \Delta p_z(\text{Sn}) < 0 \) and \( \Delta p_z(\text{Te}) > 0 \). This onsite energy differ-
In conclusion, using first-principles calculations we theoretically studied the electric structures of monolayer IV-VI semiconductors along [001] direction. Remarkably, contrary to the expectation from the quantum confinement effect, all these materials are 2D TCIs with mirror Chern number $|N_m| = 2$, and monolayer PbTe possesses the largest fundamental band gap of 260 meV. The 1D metallic edge states in these monolayer TCIs are protected by top-to-bottom mirror symmetry and robust against any perturbation preserving the mirror symmetry. The unexpected nontrivial topological phase originates from the strong asymmetric crystal field effect on $p_{x,y}$ and $p_z$ orbitals due to the unique characteristic of ultrathin 2D materials. Our work makes monolayer IV-IV semiconductors a promising materials platform to realize novel applications of topologically protected edge states, and offers a new strategy to find other 2D topologically nontrivial materials.

METHODS

The calculations were performed in the framework of first-principles density-functional theory (DFT) implemented in the Vienna $ab$ initio simulation package (VASP) [53]. We used the generalized gradient approximation (GGA) of exchange-correction function in the Perdew-Burke-Ernzerhof (PBE) form [54]. The projector augmented wave method [55] was applied to model the core electrons. Monkhorst-Pack k-point sampling of $10 \times 10 \times 1$ was used for slab calculations. Energy cutoff of the planewave basis was fully tested for all the materials, and atomic structures were optimized with maximal residual forces smaller than 0.01 eV/Å. Spin-orbit coupling (SOC) was included in all calculations.

ACKNOWLEDGEMENT

We thank Tim Hsieh for helpful discussions. This work was supported by the STC Center for Integrated Quantum Materials, NSF Grant No. DMR-1231319. X.Q. ac-
knowledges the start-up funds from Texas A&M University and the computational resources provided by Texas A&M Supercomputing Facility.

Note added: During the preparation of our manuscript, we learned of an independent work on the prediction of monolayer PbSe as TCI.

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Topological invariant is still well-defined for semimetals although the fundamental gap is negative. It is because all direct gaps are non-zero in the whole Brillouin zone, separating the bands into the lower manifold and the higher manifold. Therefore, all the states in the lower bands form a closed manifold and allow us to define the corresponding mirror Chern number. From this sense and for the sake of the simplicity, we still name them as TCIs.

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SUPPLEMENTARY MATERIALS

In the Supporting Information, we show the band structures of all monolayer IV-VI semiconductors XY (X=Ge, Sn, Pb and Y=S, Se, Te) in details. All those materials have negative inverted gap at X point, indicating that they are nontrivial 2D topological crystalline insulators with non-zero mirror Chern number |N_m| = 2. All the GeY (Y=S, Se, Te) are semi-metals, while all other materials are semiconductors. The large fundamental gap in PbY and SnY comes from the strong spin-orbit coupling of Pb and Sn.

We define the sign of inverted gap E^X_g in all monolayer IV-VI semiconductors XY using the strain effect. We have also confirmed the nontrivial topological phases in all these materials by directly calculating the edge states.
FIG. 5. Band structures of all monolayer IV-VI semiconductors XY (X=Ge, Sn, Pb and Y=S, Se, Te).