Realizing robust large-gap quantum spin Hall state in 2D HgTe monolayer on insulating substrate

Can Qi, Liying Ouyang, and Jun Hu

School of Physical Science and Technology, Soochow University, Suzhou, Jiangsu 215006, China
Jiangsu Key Laboratory of Thin Films, Soochow University, Suzhou, Jiangsu 215006, China

Although many possible two-dimensional (2D) topological insulators (TIs) have been predicted in recent years, there is still lack of experimentally realizable 2D TI. Through first-principles and tight-binding simulations, we found an effective way to stabilize the robust quantum spin Hall state with a large nontrivial gap of 227 meV in 2D honeycomb HgTe monolayer by the $\text{Al}_2\text{O}_3$(0001) substrate. The band topology originates from the band inversion between the $s$–like and $p$–like orbitals that are contributed completely by the Hg and Te atoms, so the quantized edge states are restricted within the honeycomb HgTe monolayer. Meanwhile, the strong interaction between HgTe and $\text{Al}_2\text{O}_3$(0001) ensures high stability of the atomic structure. Therefore, the TI states may be realized in HgTe/$\text{Al}_2\text{O}_3$(0001) at high temperature.

Keywords: Topological insulator, quantum spin Hall state, honeycomb HgTe, insulating substrate

I. INTRODUCTION

Great interest in topological insulators (TIs) has been inspired in recent years, because they exhibit intriguing quantum spin Hall (QSH) states.\cite{1,2} A QSH state is characterized by the combination of insulating bulk state and quantized helical conducting edge or surface state. Here the helical conducting state provides intrinsic spin lock and is robust against elastic backscattering and localization, so that the ITs are ideal for various applications that require dissipationless spin transport.\cite{3} Although QSH band gap, but the top Sn atoms need to be iodinated.\cite{24} Zhou et al predicted that Bi or W monolayer with artificial honeycomb lattice on halogen decorated Si(111) surface also exhibits large nontrivial band gap.\cite{25} However, these systems may be difficult to be produced in experiment, because of the delicate atomic structures.

For a chemically bound system with a 2D TI and an insulating substrate, the strong hybridization mainly occurs between the vertically aligned orbitals, such as the $s$ and $p_z$ orbitals. Therefore, the QSH state will be destroyed if it originates from the $p_z$ orbital such as in graphene and silicene. In contrast, the in-plane $p_x$ and $p_y$ orbitals do not interact strongly with the substrate. Accordingly, the QSH state may be preserved if it derives from the $p_x$ and $p_y$ orbitals. Interestingly, the honeycomb HgTe and HgSe monolayer (ML) are possible candidates. Recently, it was predicted that Bi or W monolayer with artific ial honeycomb lattice on halogen decorated Si(111) surface also exhibits large nontrivial band gap.\cite{26} However, these systems may be difficult to be produced in experiment, because of the delicate atomic structures.

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In this paper, we studied the structural and electronic properties of HgTe/Al₂O₃(0001) and HgSe/Al₂O₃(0001) by using first-principles calculations and tight-binding simulations. We found that the combination of honeycomb HgTe ML and Al₂O₃(0001) can not only stabilize the atomic structure but also maintain the QSH state with a large TI gap of 227 meV, while HgSe/Al₂O₃(0001) becomes a trivial insulator with a gap. The band topology originates completely from the honeycomb HgTe ML, hence the quantized helical states are confined at the edges of the honeycomb HgTe ML. Together with the highly stable atomic structure, the QSH effect is expected to be realized in HgTe/Al₂O₃(0001) at high temperature.

II. METHODS

To model the Al₂O₃(0001) substrate, we constructed a slab of 18 atomic layers with thickness of ~11 Å, and inserted a vacuum of 15 Å between adjacent slabs. The structural and electronic properties were calculated with density functional theory (DFT) as implemented in the Vienna ab-initio simulation package. The interaction between valence electrons and ionic cores was described within the framework of the projector augmented wave (PAW) method. The fully occupied semi-core 5d orbital of Hg is treated as valence orbital. The spin-polarized local density approximation (LDA) was used for the exchange-correlation potentials and the effect of SOC was invoked self-consistently. The energy cutoff for the plane wave basis expansion was set to 500 eV. The 2D Brillouin zone was sampled by a 36×36 k-grid mesh. The atomic positions were fully relaxed with a criterion that requires the force on each atom smaller than 0.01 eV/Å.

The band topology of a system is characterized by the topological invariant $Z_2$, with $Z_2 = 1$ for TIs and $Z_2 = 0$ for ordinary insulators. For the systems without inversion symmetry, $Z_2$ can be expressed with the Berry connection and the Berry curvature as

$$Z_2 = \frac{1}{2\pi} \int \text{d}k \cdot A(k) - \int_{B^-} d^2k \mathcal{F}(k) \mod 2,$$

where $A(k) = i \sum_n \langle u_n(k) | \nabla_k u_n(k) \rangle$ is the Berry connection and $\mathcal{F}(k) = \nabla_k \times A(k)|_{z}$ is the Berry curvature; $u_n(k)$ is the the periodic part of Bloch function and the sum is over occupied bands. $B^-$ and $\partial B^-$ indicate half of 2D Brillouin zone and its boundary, respectively. The nonzero $Z_2$ invariant is an obstruction to smoothly defining the Bloch functions in $B^-$ under the time-reversal constraint. In DFT calculations, it is convenient to adopt the so-called $n$-field scheme to calculate the integration in Eq. (1). For an $N \times M$ $k$-grid mesh in the 2D Brillouin zone, the intervals along the two reciprocal vectors are $\mathbf{\mu}$ and $\mathbf{\nu}$, and $k_i$ is the vector of a grid point. Then the integer field $n(k_i)$ can be defined as

$$n(k_i) = \frac{1}{2\pi} \{[\Delta_\nu A_\mu(k_j) - \Delta_\mu A_\nu(k_j)] - \mathcal{F}(k_j)\},$$

where $\Delta_\nu$ is the forward difference operator. The $Z_2$ invariant is given by the summation of the $n$ field in half of the Brillouin zone $B^-$, i.e., $Z_2 = \sum_{k_j \in B^-} n(k_j) \mod 2$.

For a 2D TI, the band structure of its one-dimensional (1D) nanoribbon usually exhibits edge bands within the gap of the 2D TI. We used the tight-binding model as implemented in PythTB code. In general, the Hamiltonian in spin space can be written as

$$H = \begin{pmatrix} H_{\uparrow\uparrow} & H_{\uparrow\downarrow} \\ H_{\downarrow\uparrow} & H_{\downarrow\downarrow} \end{pmatrix},$$

where $\uparrow$ and $\downarrow$ stand for the up and down spins, respectively. If the SOC effect is not included, $H_{\uparrow\downarrow} = H_{\downarrow\uparrow} = 0$. For a given basis set $\{C_{i\alpha}\}$ with $i$ and $\alpha$ respectively indicating the orbital and spin, the matrix elements in Eq. (3) can be written as

$$H_{i\alpha} = \sum_{\langle j\beta \rangle} ( \delta_{i\alpha,j\beta} C_{i\alpha}^\dagger C_{j\beta} + H.C.),$$

where $\delta_{i\alpha,j\beta}$ is the hopping parameter. When $\alpha \neq \beta$, $t_{i\alpha,j\beta}$ represents the spin-flip hopping induced by the SOC effect. By using the Wannier90 code, the maximally localized Wannier functions (MLWFs) can be obtained based on the DFT calculations. Then, the hopping parameter between any two orbitals can be calculated with the MLWFs.

III. RESULTS AND DISCUSSIONS

We first investigated the structural and electronic properties of the freestanding honeycomb HgTe ML which can be regarded as the HgTe(111) surface with only two atomic layers as shown in Fig. 1(a). To obtain the optimal lattice constant, we calculated the total energy as a function of lattice constant as plotted in Fig. 1(b). It can be seen that the ground state locates at $a = 4.61$ Å which is slightly larger than the lattice constant of HgTe(111) ($a = 4.57$ Å). The honeycomb HgTe ML keeps buckled with buckling distance of 0.48 Å and Hg-Te bond length of 2.8 Å as listed in Table I. This is different from other zinc blend semiconductors whose ultrathin (111) surface prefers planar honeycomb structure.

| $d_1$ | $d_2$ | $d_3$ | $\Delta h$ | $\theta$ | $E_b$ |
|-------|-------|-------|-----------|--------|------|
| FS    | 2.80  | 3.54  | 3.46      | 0.42   | 117.8|
| Type-I| 2.87  | 2.74  | 2.70      | 0.84   | 111.9|
| Type-II| 2.78  | 3.54  | 3.46      | 0.42   | 117.8|

TABLE I. The structural properties of freestanding (FS) and Al₂O₃(0001) supported (type-I and type-II) honeycomb HgTe ML. Different bond lengths ($a$ Å), the buckling distance (in Å) and the inner angles (in degree) are indicated in Fig. 1 and 3. The binding energy is calculated as $E_b = E(HgTe) + E[Al₂O₃(0001)] - E[HgTe/Al₂O₃(0001)]$. 


Then we calculated the band structures without and with considering the SOC effect, respectively. As displayed in Fig. 1(c) and 1(d), without considering the SOC effect, the honeycomb HgTe ML is a semi-metal with a Dirac cone at the \( \Gamma \) point. When the SOC is involved, a large band gap of 200 meV is induced at the \( \Gamma \) point. To reveal the orbital characters of the states near the Fermi level \( (E_F) \) at the \( \Gamma \) point, we projected the band structures onto the atomic orbitals of the Hg and Te atoms. Note that the \( p_x \) and \( p_y \) orbitals are degenerate (notated as \( p_{xy} \)) due to the local \( C_{3v} \) symmetry. As shown in Fig. 2(a–d), the \( p_z \) orbital of both Hg and Te atoms does not contribute to states near \( E_F \) at the \( \Gamma \) point. In fact, the Dirac-like bands around the \( \Gamma \) point are dominated by the \( \text{Hg}−s \) and \( \text{Te}−p_{x,y} \) orbitals, while the parabolically dispersive band is mainly from the \( \text{Te}−p_{x,y} \) orbital. To elucidate the evolution of the atomic orbitals, we extracted the energy levels at the \( \Gamma \) point and plotted in Fig. 2(c). The chemical bonding between the Hg and Te atoms turns s and \( p_{xy} \) into the bonding orbitals \((s^−, |p_{xy}^−|)\) and antibonding orbitals \((s^+, |p_{xy}^+|)\). It is clear that \( s^− \) and \( p_{xy}^− \) couple with the bands near the Fermi level \( (E_F) \). In the absence of SOC, the energy level of \( |s^−| \) locates above that of \( |p_{xy}^+| \), resulting in a normal band order. After the SOC effect is taken into account, \( |p_{xy}^+| \) further splits into \( |p_{\pm3/2}^+| \) and \( |p_{\pm1/2}^+| \), with the former shifting upwards and the later downwards. Moreover, \( |s^−| \) and \( |p_{xy}^+| \) couple with each other through the SOC Hamiltonian, which reduces the energy level of \( |s^−| \). As a consequence, the energy levels of \( |s^−| \) and \( |p_{xy}^+| \) invert at \( \Gamma \) point, implying nontrivial band topology. Accordingly, we calculated the \( Z_2 \) invariant with the \( n \)-field method. By summing the positive and negative \( n \) field numbers in half of the Brillouin zone shadow area in the inset in Fig. 2(f), we obtained \( Z_2 = 1 \), clearly demonstrating the nontrivial band topology of the honeycomb HgTe.

It is known that the TIs are manifested by quantized edge states which can be seen in the band structure of the corresponding 1D nanoribbons. Therefore, we applied tight-binding model to calculate the band structure of a 1D HgTe nanoribbon. We should point out that if only the low-energy bands near \( E_F \) are considered, a four-band model with only the first nearest neighboring hopping between the \( s \) and \( p_{xy} \) orbitals of Hg and Te is a good approximation. In our calculation, however, we considered all the hopping with \(|t_{ij\alpha\beta}| > 0.001 \text{ eV}\), which includes interactions up to the sixth nearest neighbors. The hopping parameters have been tested rigorously, and the tight-binding model precisely reproduces the DFT band structures (see Fig. S1). A 1D HgTe nanoribbon with zigzag edges and width of 60 unit cells \((D = 60 \text{ u.c.})\) was chosen, and its band structure is plotted in Fig. 3(a). Apparently, linearly dispersive bands appear in the gap of the 2D honeycomb HgTe ML. Since a wavefunction is
the linear combination of all the atomic orbitals with coefficient $C_{i\alpha} \sum_{\alpha} |C_{i\alpha}|^2$ over the orbitals of a single atom gives the atomic weight $w_{\alpha}$ from which we can obtain the spatial distributions of the wavefunctions. As shown in Fig. 3(b) for the ‘A’ and ‘B’ points, the wavefunctions of both bands are localized in the edge region on the same side, and the Te $p_{xy}$ orbitals dominate the wavefunctions. From $C_{i\alpha}$, we found that the bands crossing ‘A’ and ‘B’ carry the spin-up and spin-down electrons, respectively. In addition, these bands have opposite slopes, which indicates that the spin-up and spin-down electrons propagate along opposite directions on the edge. Similarly, the other two bands (red and blue) in the inset in Fig. 3(b) carry the spin-up and spin-down electrons on the other side of the HgTe nanoribbon. Therefore, these edge bands provide the helical edge states for the QSH effect.

Then we put the honeycomb HgTe ML on Al$_2$O$_3$(0001) ($a = 4.76$ Å) which imposes extensile strain of 3.2% on the honeycomb HgTe ML. There are two adsorption configurations for the honeycomb HgTe ML. Fig. 4 shows the type-I configuration: the Hg atom locates over the center of three surface O atoms and the Te atom is above the surface Al atom. Switching the positions of the Hg and Te atoms yields the type-II configuration. It can be seen from Table I that the Hg-Te bond lengths in both configurations do not change much from those of the freestanding honeycomb HgTe ML. The binding between the HgTe and Al$_2$O$_3$(0001) is strong in the type-I configuration, resulting in short O-Hg and Al-Te bond lengths, higher buckling distance (0.84 Å), and large adsorption energy (0.99 eV), as listed in Table I. The honeycomb HgTe ML is physisorbed on Al$_2$O$_3$(0001) in the type-II configuration, so that the O-Te and Al-Hg bond lengths are large and the adsorption energy is small (0.04 eV). Therefore, it is most probable to obtain the type-I configuration when growing honeycomb HgTe ML on Al$_2$O$_3$(0001).

It is interesting to see how the electronic structure of the honeycomb HgTe ML changes with the interaction from Al$_2$O$_3$(0001) substrate. Hence we calculated the band structure of the type-I HgTe/Al$_2$O$_3$(0001). It can be seen from Fig. 4(b) and 4(c) that the bands locating in the gap of Al$_2$O$_3$(0001) ($\approx 0.8 \sim 4.0$ eV) originate from HgTe completely. As indicated by the orbital-resolved bands in Fig. 4(c) and 4(d), the Dirac-like bands that cross $E_F$ are contributed by the Hg–s and Te–$p_{x,y}$ orbitals, while the parabolically dispersive band below $E_F$ is mainly from Te–$p_{x,y}$. These characters are similar to those in the freestanding honeycomb HgTe ML. In the absence of SOC, HgTe/Al$_2$O$_3$(0001) is a semimetal with a Dirac cone at $\Gamma$ point. When the SOC effect is included, a large band gap of 227.2 meV opens at the Dirac point with $E_F$ locating in the gap. The SOC also mediates the interaction between the Hg–s and Te–$p_{x,y}$ orbitals, leading to the band inversion near $E_F$ at $\Gamma$ point, as shown in Fig. 4(f) and 4(g). Therefore, HgTe/Al$_2$O$_3$(0001) maintains the basic electronic features of the freestanding honeycomb HgTe ML, which implies the nontrivial band topology in the type-I HgTe/Al$_2$O$_3$(0001).

To confirm the topological character of the type-I HgTe/Al$_2$O$_3$(0001), we calculated the $Z_2$ invariant with
the n-field method. From the n-field configuration in Fig. 5(a), we obtained $Z_2 = 1$, which is the clear evidence for nontrivial band topology. This can be further demonstrated by the band structure and atomic structure of 1D type-I HgTe/Al$_2$O$_3$(0001) nanoribbon with zigzag edges. The actual width of the 1D nanoribbon in calculation is 50 u.c. The horizontal dashed line represents the Fermi level. The long arrows in (c) indicate the directions of the edge currents. The short arrows denote the spin-up (red) and spin-down (blue) electrons, respectively.

In the realistic growth environment, it is possible to get the type-II HgTe/Al$_2$O$_3$(0001) [Fig. 6(a)] in equilibrium condition, although it has much smaller binding energy than that of the type-I configuration. Therefore, we calculated the corresponding band structures as displayed in Fig. 6(d) and 6(e). It is clear that the energy bands near $E_F$ are quite different from those of the freestanding honeycomb HgTe ML, because of the interaction between HgTe and Al$_2$O$_3$(0001), although the interaction is weak. Nevertheless, the band orders at the $\Gamma$ point are the same as those of the type-I HgTe/Al$_2$O$_3$(0001) (see Fig. S3). Furthermore, the band structures clearly show that the SOC opens a band gap of 171 meV near $E_F$. Interestingly, this gap is also topologically nontrivial, which can be manifested by the nonzero $Z_2$ invariant ($Z_2 = 1$) in Fig. 6(b) and the quantized edge states in the bulk gap in Fig. 6(c). This is good for experimental realization and investigation of the QSH effect in HgTe/Al$_2$O$_3$(0001), because the exact configuration of the atomic structure is not a exclusive precondition to realize the nontrivial topological insulator states in HgTe/Al$_2$O$_3$(0001).

Another factor to hinder the realization of the QSH effect in HgTe/Al$_2$O$_3$(0001) is that the thickness of HgTe is more than one monolayer, which may ruin band topology. Therefore, we calculated the band structures of HgTe/Al$_2$O$_3$(0001) with two MLs of HgTe as shown in Fig. S4. We found that the type-I structure becomes metallic with two MLs of HgTe on Al$_2$O$_3$(0001) no matter the SOC effect is included or not. In contrast, the type-II structure maintains topologically nontrivial. However, the binding energy of the type-II structure is 0.78 eV larger than that of the type-I structure, so the possibility to get the type-I structure is much larger than the type-
II structure. Therefore, the thickness of HgTe should be restricted to one monolayer to realize and investigate the QSH effect in HgTe/Al₂O₃(0001).

With the large topological insulator gap in the type-I HgTe/Al₂O₃(0001), it is expected to observe the QSH effect at high temperature. Therefore, it is important to investigate the thermal stability of the atomic structure of HgTe/Al₂O₃(0001). To this end, we carried out ab initio molecular-dynamics simulation at 300 K. We found that the binding between HgTe and Al₂O₃(0001) keeps strong, so that the HgTe ML does not detach or drift on Al₂O₃(0001). Furthermore, the HgTe monolayer maintains the honeycomb structure against the thermal vibration at 300 K (see Fig. S5). This suggests that HgTe/Al₂O₃(0001) can survive at room temperature and the QSH effect may be observed. Furthermore, the QSH state of HgTe/Al₂O₃(0001) may be robust under some other factors such as the moderate external electric field, because the insulating Al₂O₃(0001) substrate can effectively prevent further charge transfer between HgTe and Al₂O₃(0001). In contrast, the external electric field significantly affects the QSH state in CdTe/HgTe/CdTe quantum well.²⁹

IV. CONCLUSION

In summary, we proposed a robust QSH insulator which is composed of low buckled honeycomb HgTe monolayer and α−Al₂O₃(0001), based on first-principles and tight-binding simulations. The analyses of the electronic structures reveal that HgTe/Al₂O₃(0001) is topologically nontrivial with nonzero topological invariant \( Z₂ = 1 \). The topological insulator gap is as large as 227 meV. The band topology is caused by the band inversion between the energy levels of \( |s⁻\rangle \) and \( |pₓ^+\rangle \) of the Hg and Te atoms. Interestingly, both the ground-state and metastable structures are topologically nontrivial and the atomic structures are stable at high temperature. Furthermore, the insulating substrate not only supports and stabilizes HgTe, but also protects the helical edge states against electronic contamination from substrate. These features are beneficial to experimental realization of the QSH effect at relatively high temperature. Our strategy paves the way for engineering realistic 2D TI which may be achieved in experiment and used for real applications at room temperature.

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*E-mail: jhu@suda.edu.cn

1. Kane C L and Mele E J 2005 Phys. Rev. Lett. 95 146802.
2. Bernevig B A and Zhang S C 2006 Phys. Rev. Lett. 96 106802.
3. Bernevig B A, Hughes T L and Zhang S C 2006 Science 314 1757–1761.
4. Nagaosa N 2007 Science 318 758–759.
5. König M, Wiedmann S, Brüne C, Roth A, Buhmann H, Molenkamp L W, Qi X L and Zhang S C 2007 Science 318 766–770.
6. Hasan M Z and Kane C L 2010 Rev. Mod. Phys. 82 3045–3067.
7. Qi X L and Zhang S C 2011 Rev. Mod. Phys. 83 1057–1110.
8. Weekes C, Hu J, Alicea J, Franz M and Wu R Q 2011 Phys. Rev. X 1 021001.
9. Hu J, Alicea J, Wu R Q and Franz M 2012 Phys. Rev. Lett. 109 266801.
10. Hu J, Zhu Z Y and Wu R Q 2015 Nano Lett. 15 2074–2078.
11. Fu L and Kane C L 2007 Phys. Rev. B 76 045302.
12. Hsieh D, Qian D, Wray L, Xia Y, Hor Y S, Cava R J and Hasan M Z 2008 Nature 452 970–974.
13. Zhang H J, Liu C X, Qi X L, Dai X, Fang Z and Zhang S C 2009 Nat. Phys. 5 438–442.
14. Xia Y, Qian D, Hsieh D, Wray L, Pal A, Lin H, Bansil A, Grauer D, Hor Y S, Cava R J and Hasan M Z 2009 Nat. Phys. 5 398–402.
15. Chen Y L, Analytis J G, Chu J H, Liu Z K, Mo S K, Qi X L, Zhang H J, Lu D H, Dai X, Fang Z, Zhang S C, Fisher I R, Hussain Z and Shen Z X 2009 Science 325 178–181.
16. Liu C, Hughes T L, Qi X L, Wang K and Zhang S C 2008 Phys. Rev. Lett. 100 236601.
17. Knez I, Du R R and Sullivan G 2011 Phys. Rev. Lett. 107 136603.
18. Du L, Knez I, Sullivan G and Du R R 2015 Phys. Rev. Lett. 114 096802.
19. Qian X F, Liu J W, Fu L and Li J 2014 Science 346 1344–1347.
20. Weng H, Dai X and Fang Z 2014 Phys. Rev. X 4 011002.
21. Chuang F C, Yao L Z, Huang Z Q, Liu Y T, Hsu C H, Das T, Lin H and Bansil A 2014 Nano Lett. 14 2505–2508.
22. Ma Y, Dai Y, Kou L, Frauenheim T and Heine T 2015 Nano Lett. 15 1083–1089.
23. Li L Y, Zhang X M, Chen X and Zhao M W 2015 Nano Lett. 15 1083–1089.
24. Liu C C, Feng W X and Yao Y G 2011 Phys. Rev. Lett. 107 126802.
25. Vogt P, Padova P D, Quaresima C, Avila J, Frantzeskakis E, Asensio M C, Resta A, Ealat B and Lay G L 2012 Phys. Rev. Lett. 108, 155501.
26 Meng L, Wang Y, Zhang L, Du S, Wu R, Li L, Zhang Y, Li G, Zhou H, Hofer W A and Gao H J 2013 Nano Lett. 13 685–690.
27 Xu Y, Tang P and Zhang S C 2015 Phys. Rev. B 92 081112.
28 Wang H, Pi S T, Kim J, Wang Z, Fu H H and Wu R Q 2016 Phys. Rev. B 94 035112.
29 Zhou M, Ming W, Liu Z, Wang Z, Lia P and Liu F 2014 Proc. Natl. Acad. Sci. USA 111 14378.
30 Zhou M, Liu Z, Ming W, Wang Z and Liu F 2014 Phys. Rev. Lett. 113 236802.
31 Li J, He C, Meng L, Xiao H, Tang C, Wei X, Kim J, Koussis N, Stocks G M and Zhong J 2015 Sci. Rep. 5 14115.
32 Li S S, Ji W X, Zhang C W, Lia P and Wang P J 2016 J. Mater. Chem. C 4 2243–2251.
33 Tusche C, Meyerheim H L and Kirschner J 2007 Phys. Rev. Lett. 99 026102.
34 Al Balushi Z Y, Wang K, Ghosh R K, Vilá R A, Eichfeld S M, Caldwell J D, Qin X, Lin Y C, DeSario P A, Stone G, Subramanian S, Paul D F, Wallace R M, Datta S, Redwing J M and Robinson J A 2016 Nat. Mater. 15 1166–71.
35 Kresse G and Furthmüller J 1996 Comput. Mater. Sci. 6 15–50.
36 Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169–11180.
37 Blöchl P E 1994 Phys. Rev. B 50 17953–17979.
38 Kresse G and Joubert D 1999 Phys. Rev. B 59 1758–1775.
39 Perdew J P and Zunger A 1981 Phys. Rev. B 23 5048–5079.
40 Fu L and Kane C L 2006 Phys. Rev. B 74 195312.
41 Fukui T and Katsugai Y 2007 J. Phys. Soc. Jpn. 76 053702.
42 Xiao D, Yao Y, Feng W, Wen J, Zhu W, Chen X Q, Stocks G M and Zhang Z 2010 Phys. Rev. Lett. 105 096404.
43 Feng W, Wen J, Zhou J, Xiao D and Yao Y 2012 Comput. Phys. Commun. 183 1849.
44 PythTB, by S.Coh and D.Vanderbilt, available at http://www.physics.rutgers.edu/pythtb/index.html
45 Mostofi A A, Yates J R, Pizzi G, Lee Y S, Souza I, Vanderbilt D and Marzari N 2014 Comput. Phys. Commun. 185 2309.
46 Marzari N and Vanderbilt D 1997 Phys. Rev. B 56 12847.
47 Souza I, Marzari N and Vanderbilt D 2001 Phys. Rev. B 65 035109.
48 Freeman C L, Claeyssens F, Allan N L and Harding J H 2006 Phys. Rev. Lett. 96 066102.
49 Sengupta P, Kubis T, Tan T, Povolotskyi M and Klimeck G 2013 J. Appl. Phys. 114 043702.