Two- and three-dimensional topological phases in BiTeX compounds

S. V. Eremeev,^{1,2,3,4} I. A. Nechaev,^{5,1,2} and E. V. Chulkov^{5,1,2,4,6}¹Tomsk State University, 634050 Tomsk, Russia²Saint Petersburg State University, 198504 Saint Petersburg, Russia³Institute of Strength Physics and Materials Science, 634055 Tomsk, Russia⁴Donostia International Physics Center, 20018 San Sebastián/Donostia, Spain⁵Centro de Física de Materiales CFM-MPC and Centro Mixto CSIC-UPV/EHU, 20018 San Sebastián/Donostia, Spain⁶Departamento de Física de Materiales UPV/EHU, Facultad de Ciencias Químicas, UPV/EHU, Apdo. 1072, 20080 San Sebastián/Donostia, Spain

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Recently, it was shown that quantum spin Hall insulator phase with a gap wide enough for practical applications can be realized in the ultrathin films constructed from two inversely stacked structural elements of trivial band insulator BiTeI. Here, we study the edge states in nanoribbons made of the Bi₂Te₂I₂ sextuple layer (SL) and the electronic structure of the SL deposited on the natural BiTeI substrate as well as sandwiched between two thick BiTeI films. We show that the Bi₂Te₂I₂ SL keeps nontrivial topological properties. We also demonstrate that ultrathin centrosymmetric films constructed in a similar manner from related material BiTeBr are trivial band insulators up to five-SL film thickness. In contrast to Bi₂Te₂I₂ for which the stacking of nontrivial SLs in a three-dimensional (3D) limit results in a strong topological insulator (TI) phase, a 3D TI Bi₂Te₂Br₂ is formed by trivial SLs. For the last material of the BiTeX (X = I, Br, Cl) series, BiTeCl, both 2D and 3D centrosymmetric phases are characterized by topologically trivial band structure.

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I. INTRODUCTION

Starting from the theoretical predictions by Kane and Mele [1] and Bernevig *et al.* [2,3], the $\mathbb{Z}_2$ two-dimensional topological insulator (2D TI) or the quantum spin Hall insulator (QSHI) phase, in which spin-helical gapless edge states counterpropagate along the boundary with opposite spins, providing quantum spin Hall effect (QSHE) [1], attracts considerable attention of researchers. After experimental observations of the QSHE in HgTe/CdTe and InAs/GaSb quantum wells [4,5], a number of 2D TIs were theoretically proposed [6]. These proposals were mainly based on the layers of bismuth, graphene, or heavy elements analogs of graphene, implying the gap tuning by strain, adatoms deposition, chemical functionalization, growing on substrates, or sandwiching. In contrast to 3D TIs, for which the existence of topologically protected Dirac surface states was found in a wide variety of materials, the edge states in 2D TIs by now were directly observed experimentally in a limited number of systems like Bi(111)-bilayer islands on a Bi-crystal surface [7], Bi(110) [8] and Sb(111) [9] thin films, and step edges in ZrTe₅ [10,11] and Bi₁₄Rh₃I₉ [12,13]. The QSHE was also confirmed in the quantum wells with tiny band gaps only [6], where a topologically protected state does not survive at temperatures above 10 K. Thus the goal that remains to be actual so far is to search for robust and easily fabricated new 2D TIs with a sufficiently large band gap providing edge states accessible to experimental probes at room temperature.

Recently, a distinct way to design novel topological systems on the base of two-dimensional materials consisting of layered band insulators was suggested [14]. It was demonstrated that these systems can be realized under normal conditions in thin films comprising van der Waals coupled structure elements [trilayers (TLs)] of the giant-Rashba semiconductor BiTeI, which belongs to the intensively investigated chalcogenides BiTeX (X = Cl, Br, and I) [15–34].

BiTeX compounds have a hexagonal noncentrosymmetric crystal structure built of ionically bonded X-Bi-Te TL stacked along the hexagonal z axis. In addition to the large bulk and surface Rashba splitting in these materials, a single BiTeX trilayer holds the giant Rashba-split states as well [35]. Among BiTeX materials, BiTeI demonstrates the largest bulk Rashba splitting [15,16,22], while BiTeCl stands out for its isotropic spin-split metallic surface state lying deep inside the bulk band gap [16], which is the biggest one in the BiTeX series. Generally, the BiTeX surfaces, which can be Te or X terminated, can possess, respectively, an electron- or holelike Rashba-split surface state that emerges by splitting off from the lowest conduction (highest valence) band, owing to the negative (positive) surface potential bending [16]. However, it turned out that the surface of BiTeI obtained by natural cleavage of single crystals grown by the Bridgman method always holds both types of the surface states due to Te- and I-terminated domains, inhomogeneously distributed over the surface [17,18,26,27,29,31,33]. These surface domains are the consequence of a large number of randomly distributed bulk stacking faults, in which the TLs stacking order is inverted [29,31,33]. The calculated bulk stacking fault formation energy in the BiTeI bulk, 1 meV, is much smaller than for BiTeBr (46 meV) and BiTeCl (60 meV) [31] that explains the existence of the mixed domain termination on the BiTeI surface in contrast to the BiTeBr and BiTeCl (0001) surfaces characterized by single polar domains.

It was demonstrated [14] that a centrosymmetric sextuple layer (SL) constructed from two BiTeI TLs with facing Te-layer sides is a 2D TI with the inverted gap of about 60 meV at $\bar{\Gamma}$, which can be sufficiently enough for room temperature spintronics applications. Due to the bonding-antibonding splitting, the gap inversion occurs between one of the Te-related valence bands (VBs) and one of the conduction bands (CBs) formed by Bi orbitals. The centrosymmetric BiTeI films

demonstrate rapid decrease in the gap width with the increase of the number of SLs along with oscillating behavior in the $\mathbb{Z}_2$ topological invariant like in thin films of the Bi_2Te_3 family (see, e.g., Refs. [36–39]). The corresponding bulk system composed of SLs turned out to be a strong 3D TI (hereafter referred to as $\text{Bi}_2\text{Te}_2\text{I}_2$). It is energetically unfavorable by only 0.5 meV compared with the noncentrosymmetric BiTeI . It should be noted that due to the stacking faults mentioned above crystals of BiTeI grown by the Bridgman method already contain the desired SLs, and that the inverted stacking can be experimentally observed and controllably manufactured.

Most of the earlier theoretically predicted 2D TIs were considered as free-standing systems. However, for practical applications, a freestanding 2D TI must be placed or grown on an appropriate substrate which, in general, will influence the intrinsic topological properties of thin films due to interfacial and proximity effects [40] such as mismatch in the lattice constants and charge transfer at the interface of diverse materials [41–45]. Therefore, suitable substrates to support room-temperature TIs are important for potential device applications. Several 2D TI systems, mostly Bi-based layers on silicon substrate, were theoretically suggested [46–52]. However, they have not been experimentally realized up to now. The exception is the honeycomb Bi on $\text{Au/Si}(111)$ - $(\sqrt{3}\times\sqrt{3})$ and SiC substrates, which was successfully grown as confirmed by STM measurements [52,53]. Nevertheless, the QSHE has not been proved to be observable in this system so far. In this regard, the 2D TI $\text{Bi}_2\text{Te}_2\text{I}_2$ -SL has a significant advantage, since it has a natural substrate—the noncentrosymmetric BiTeI band insulator, which guarantees an absence of both lattice mismatch and interface charge transfer effects, since there is no work function difference between the substrate and the 2D TI adlayer.

In this paper, using first-principles electronic structure calculations, we examine the edge states of the $\text{Bi}_2\text{Te}_2\text{I}_2$ 2D TI of one-SL thickness for different edge orientations. We consider the effect of the BiTeI substrate on the electronic structure of this 2D TI and show that SL remains topologically nontrivial. Additionally we examine the topology of the electronic structure of the SL sandwiched between two thick BiTeI films. Finally, we study the topological properties of the related 2D and 3D centrosymmetric phases $\text{Bi}_2\text{Te}_2\text{Br}_2$ and $\text{Bi}_2\text{Te}_2\text{Cl}_2$.

II. METHODS

Calculations were carried out within generalized gradient approximation (GGA) with the projector augmented-wave method [54,55] as realized in the Vienna Ab Initio Simulation Package (VASP) [56,57]. DFT-D3 van der Waals (vdW) correction [58] was applied for accurate structure optimization. Bulk lattice parameters and atomic positions of $\text{Bi}_2\text{Te}_2\text{X}_2$ phases [the 164 ($P\bar{3}m1$) space group] were optimized. The optimized parameters a and c for bulk $\text{Bi}_2\text{Te}_2\text{I}_2$ have been obtained to be 4.354 and 13.421 Å, respectively, and they have been found to be 4.474 and 11.676 Å for $\text{Bi}_2\text{Te}_2\text{Br}_2$ and 4.288 and 12.155 Å for $\text{Bi}_2\text{Te}_2\text{Cl}_2$. For all $\text{Bi}_2\text{Te}_2\text{X}_2$ bulk phases, the a parameter is slightly larger than that in respective noncentrosymmetric BiTeX compounds. The Bi-Te and Bi-X interlayer spacings in $\text{Bi}_2\text{Te}_2\text{X}_2$ bulk are also close to those in BiTeX ; Te – Te(X - X) interlayer distances in

FIG. 1. Atomic structure of the $\text{Bi}_2\text{Te}_2\text{I}_2$ one-SL film (a) with its top view (b) and side views in yz and xz planes [(c) and (d), respectively]. e_1 and e_2 dashed lines (red and blue, respectively) show cleavage planes for considered stoichiometric edges. Light-gray rhombus and magenta rectangle in (b) mark the unit cell and related rectangular cell by repeating of which in x or y direction we construct different nanoribbons. (e) Band structure of the free-standing $\text{Bi}_2\text{Te}_2\text{I}_2$ SL along $\bar{\Gamma} - \bar{K}$ and $\bar{\Gamma} - \bar{M}$ directions of the 2D hexagonal Brillouin zone (BZ); yellow stripe shows the region of the band inverted gap. Red and blue circles show the hidden spin polarization [62] calculated as in-plane spin projection onto the upper half of the SL. Black hexagon in (f) shows 2D hexagonal BZ; red rectangle shows 2D BZ for rectangular cell and blue lines indicate its projections onto 1D BZs along k_x and k_y axes.

$\text{Bi}_2\text{Te}_2\text{X}_2$ bulk phases vary in the range of $X = \text{I, Br, and Cl}$ as 2.655(3.094), 2.456(2.521), and 2.796(2.623) Å. For single free-standing $\text{Bi}_2\text{Te}_2\text{X}_2$ SLs, we performed additional structural optimization. A small contraction (expansion) was obtained for the Te-Te distance (the outer Bi- X spacing), while Te-Bi interlayer spacing remained unchanged as compared to the respective bulk values. The $\mathbb{Z}_2$ topological invariant was

FIG. 2. (a) Atomic structure of the e_1 edge. (b) Electronic spectrum and spin polarization for localized states at the edge; red/blue circles represent positive/negative sign of the spin component for localized states. (c) Atom-projected localization of the trivial dangling bond states as calculated with the switched off SOC. (d) Electronic structure of the e_1 edge of the topologically trivial $\text{Bi}_2\text{Te}_2\text{I}_2$ film with vdW spacing expanded by 10%. Orbital character of the localized states for Bi (left panel) and Te (right panel) contributions for the trivial (vdW+10%) system (e) and the $\text{Bi}_2\text{Te}_2\text{I}_2$ QSH insulator (f).

calculated by using the method based on tracking the evolution of hybrid Wannier functions realized in Z2Pack [59].

III. RESULTS AND DISCUSSION

A. Edge states in $\text{Bi}_2\text{Te}_2\text{I}_2$ -SL nanoribbons

First we studied the energies of edges with different geometry to find out the most stable edge for the $\text{Bi}_2\text{Te}_2\text{I}_2$ -SL nanoribbon. We have considered stoichiometric mutually perpendicular cleavage planes e_1 and e_2 ; see Figs. 1(b)–1(d). The e_1 plane is parallel to the $[\bar{1}100]$ (x) axis and crosses (0001) (xy) plane at an angle of 56.96° . The e_2 plane is parallel to the $[11\bar{2}0]$ (y) axis and passes perpendicular to the (0001) plane. As expected from the effective continuous model [60], the decay depth of the topological edge states in 2D TI should be much larger than that for the Dirac surface states in 3D TI. Consequently, to avoid the finite size effect, the nanoribbon width should be chosen as large as possible. We have constructed nanoribbons bounded by the two parallel e_1 and e_2 cleavage planes of the width of $\sim 150 \text{ \AA}$. We found that the e_1 edge is by $\sim 170 \text{ meV/\AA}^2$ more favorable than the e_2 one. The stability of the e_1 edge looks reasonable, because the preferred cleavage plane is the one which minimizes the number of broken bonds. The square of the e_1 plane is about 1.5 times smaller than that of the e_2 plane, while the number of broken bonds at the e_2 plane is two times bigger as compared to e_1 (8 and 4, respectively), and thus the density of the broken

bonds (per unit square) is smaller for the e_1 edge. Note that the stoichiometric cleavage plane, similar to e_1 , was found to be stable for the $\text{Bi}_2\text{Te}(\text{Se})_3$ single quintuple layer (QL) [61].

Next, we examine the electronic structure of the ribbons with the e_1 and e_2 edges. Figure 1(e) shows the spectrum of the $\text{Bi}_2\text{Te}_2\text{I}_2$ film of single SL thickness calculated along high-symmetry directions of the hexagonal Brillouin zone [Fig. 1(f)]. As was demonstrated in Ref. [14] this film has an inverted gap of $\sim 60 \text{ meV}$ at the Fermi level, and in this gap (yellow stripe) we expect to find one-dimensional topological spin-helical states localized at the edge of the nanoribbon. When the e_1 (e_2) edge is formed, the 2D BZ of the SL is projected onto 1D BZ along the k_x (k_y) direction [Fig. 1(f)].

The calculated electronic structure of the e_1 ribbon [Fig. 2(a)] is shown in Fig. 2(b), where left and right panels demonstrate the same electronic spectrum but different projections of the spin expectation value for the localized states, S_y and S_z , which are orthogonal to the wave vector k_x (S_x component of the spin is zero). They are calculated as a sum over atomic contributions from five near-edge atomic layers. As seen in Fig. 2(b), the spectrum has a gap at the Dirac point (of few meV) as the result of hybridization between edge states localized at the opposite edges of the ribbon despite the fact that we have chosen quite wide ribbon. Another observation is that beside the $\bar{\Gamma}$ Dirac state the band structures also show the presence of a number of spin-polarized resonant states mainly in the valence band region as well as two trivial

FIG. 3. Atomic structure (a) and electronic spectrum with spin polarization (b) for the e_2 edge of $\text{Bi}_2\text{Te}_2\text{I}_2$ nanoribbon.

Rashba-split dangling bond states in the gap region far from the $\bar{\Gamma}$ point. These states are originated from the broken bonds at the edge. With switched off spin-orbit coupling (SOC) these dangling bond states appear as two almost dispersionless bands [Fig. 2(c)]. The occupied and unoccupied bands have only small iodine contribution and the former band is mainly contributed by Te orbitals, while the latter is primarily formed by Bi orbitals. Both these bands have p_{yz} character over the 1D BZ that reflects the fact the dangling bonds are oriented perpendicular to the e_1 cleavage plane.

As was shown in Ref. [14], the vdW interaction between TLs in the SL is crucial to realize the QSHI phase. The gap in the SL spectrum closes at increasing the vdW spacing by 5% and further increase in the vdW spacing opens a trivial gap. At 10% expansion, the spectrum has the trivial gap of the width comparable to that in the equilibrium band-inverted SL [14]. Constructing the nanoribbon with the vdW spacing expanded by 10%, we found merely two dangling bond states acquired the Rashba splitting [Fig. 2(d); S_y spin component is only shown]. At large k_x ($>0.3 \text{ \AA}^{-1}$) despite the spin splitting both bands keep their p_{yz} character, whereas at small k_x [Fig. 2(e)] the orbital character is changed due to emergence of p_x orbitals and the appearance of Bi p_{yx} states in the occupied band along with Te p_x states in the unoccupied band. Comparing the orbital character of the Rashba-split dangling bond states near the $\bar{\Gamma}$ point at the edge in trivial (vdW-expanded) SL with that in the QSHI [Fig. 2(f)], one can conclude that the emergent Dirac states have the atom-type contributions and the orbital compositions similar to that of trivial states, which strongly hybridize with the Dirac state.

In the ribbon with the less stable e_2 edge [Fig. 3(a)], the spectrum and different spin projections, S_x and S_z (S_y is zero in this case), of which are presented in Fig. 3(b), additional expected trivial SO-split dangling bond states emerge in the projected gap. The number of such bands is two times larger as compared to the spectrum of the e_1 edge owing to the fact that

twice as many bonds are broken at the formation of this edge. However, as in the nanoribbon with e_1 edge, the dangling bond states lie far from the $\bar{\Gamma}$ gap region (yellow stripe) where the topological Dirac state resides.

B. $\text{Bi}_2\text{Te}_2\text{I}_2$ -SL 2D TI on BiTeI band insulator substrate

As we pointed out above, one of the main challenges for 2D TIs is appropriate substrate, and the advantage of $\text{Bi}_2\text{Te}_2\text{I}_2$ is that it has a natural substrate—BiTeI band insulator, which guarantees the absence of both the lattice mismatch and the interface charge transfer effects. Since the charge transfer is mostly a local effect, we consider first the structure composed of $\text{Bi}_2\text{Te}_2\text{I}_2$ SL and a single BiTeI TL as $[\text{I-Bi-Te-Te-Bi-I}]_{\text{SL}}-[\text{Te-Bi-I}]_{\text{TL}}$ (or simply SL-TL). The calculated band spectrum of this structure is shown in Fig. 4. As seen in Fig. 4(a), the states forming a gap in this system belong to the SL, while the states localized in the BiTeI-TL lie far from the gap edges, especially in the unoccupied part of the spectrum. Since the SL-TL system lacks the inversion symmetry, the states possess the Rashba spin splitting [Fig. 4(b)]. The splitting is almost isotropic with respect to $k_{||}$, and splitting parameters are $\Delta k = 0.026(0.020) \text{ \AA}^{-1}$ and $\Delta E = 0.048(0.029) \text{ eV}$ for valence (conduction) band. Besides the Rashba splitting of the $\text{Bi}_2\text{Te}_2\text{I}_2$ states, the gap width becomes larger. In the free-standing inversion symmetric $\text{Bi}_2\text{Te}_2\text{I}_2$ the gap is of 60 meV [Fig. 1(e)], and in the SL-TL absolute gap E_g equals 78 meV (the $\bar{\Gamma}$ gap is $E_g + \Delta E^{\text{VB}} + \Delta E^{\text{CB}}$). However, despite the Rashba splitting the gap-edge states remain inverted, as in the inversion symmetric $\text{Bi}_2\text{Te}_2\text{I}_2$ [14]. In the vicinity of $\bar{\Gamma}$, the Bi p_z orbitals are mainly localized in the valence band, while Te p_z orbitals dominate in the lowest conduction band [Fig. 4(c)]. The calculation of $\mathbb{Z}_2$ for the SL-TL structure resulted in a nontrivial topological invariant.

Next we increased the number of TLs in the slab so that the BiTeI part of the structure was sufficient to reproduce the

FIG. 4. Layer- (a) and spin-resolved (b) spectrum for $\text{Bi}_2\text{Te}_2\text{I}_2$ -SL/ BiTeI -TL film. (c) Orbital-resolved band structure in the vicinity of the $\bar{\Gamma}$ gap.

BiTeI bulk. As in earlier works [16,18,19] we used a BiTeI slab of eight-TL thickness with the back, iodine-terminated, surface passivated by hydrogen. As seen in Figs. 5(a) and 5(b), in SL@ BiTeI heterostructure the $\text{Bi}_2\text{Te}_2\text{I}_2$ states lie within the BiTeI bulk gap. The gap in $\text{Bi}_2\text{Te}_2\text{I}_2$ states $E_g = 74$ meV is almost the same as in the SL-TL case but spin-splitting parameters became slightly smaller: $\Delta k = 0.018(0.014) \text{ \AA}^{-1}$ and $\Delta E = 0.030(0.018) \text{ eV}$ for valence (conduction) band. Such small alterations in the $\text{Bi}_2\text{Te}_2\text{I}_2$ spectrum in the vicinity of $\bar{\Gamma}$ do not affect the gap inversion, Fig. 5(c). As before, the gap edges are mainly formed by p_z orbitals of Bi (VB) and Te (CB) atoms.

Thus 2D TI $\text{Bi}_2\text{Te}_2\text{I}_2$ survives on the BiTeI substrate. This is due to the fact that $\text{Bi}_2\text{Te}_2\text{I}_2$ and BiTeI are actually the same materials, which differ in TLs stacking order only. It guarantees the absence of the interface potential because the interface $[\text{I-Bi-Te-Te-Bi-I}]_{\text{SL}}-[\text{Te-Bi-I}]-[\text{Te-Bi-I}]-\dots$ can be regarded as the structure $[\text{I-Bi-Te}]-[\text{Te-Bi-I}]-[\text{Te-Bi-I}]-[\text{Te-Bi-I}]-\dots$, i.e., as the Te-terminated BiTeI surface, where the uppermost TL has inverted atomic layer sequence. The splitting in the spin subbands in the 2D TI $\text{Bi}_2\text{Te}_2\text{I}_2$ spectrum on the BiTeI substrate will result in the opposite $k_{\parallel}$ shifting of the corresponding spin branches of the Dirac state in the 1D spectrum as schematically shown in the inset in Fig. 5(b), wherein the Dirac point that is in the middle of the gap in the case of free-standing SL might be shifted downward to the region of the two-dimensional states.

We also considered the $\text{Bi}_2\text{Te}_2\text{I}_2$ SL on the opposite, I-terminated, surface of the BiTeI bulk. The SL localized states acquire the Rashba splitting similar to that on the Te-terminated surface. However, due to the large positive potential bending on the I-terminated surface, the gapped SL localized states are pushed up into the region of the BiTeI bulk conduction band, and the system thus is not relevant

anymore to nondissipative spin-polarized electron transport through their edges.

C. $\text{Bi}_2\text{Te}_2\text{I}_2$ -SL 2D TI sandwiched between two BiTeI thick films

The faults that reverse the stacking sequence of atomic planes in the bulk BiTeI and cause the experimentally observed mixed surface terminations [17,18,26,27,29,31] can be modeled by pairs of BiTeI thick films with facing Te- or I-layer sides. The Te-Te interface region of a pair thus naturally contains the SL under study. To examine the electronic structure of the SL built into such a BiTeI environment we start with a minimal structural model. This structure contains the SL and two adjacent BiTeI TLs as $[\text{I-Bi-Te}]_{\text{TL}}-[\text{I-Bi-Te-Te-Bi-I}]_{\text{SL}}-[\text{Te-Bi-I}]_{\text{TL}}$ (or simply $\text{TL}'\text{-SL-TL}$, where prime symbol means the inverted atomic layer sequence in the TL). The $\text{TL}'\text{-SL-TL}$ structure differs from the considered above SL-TL film in that it possesses the inversion symmetry and as a result its spectrum presented in Fig. 6(a) demonstrates twofold degenerate bands with hidden spin polarization [Fig. 6(b)] similar to that in the free-standing SL [Fig. 1(e)]. However, as in the inversion asymmetric film the gap edges are determined by the inverted Bi p_z and Te p_z orbitals of the SL. The calculated $\mathbb{Z}_2$ invariant for $\text{TL}'\text{-SL-TL}$ structure is equal to unity, confirming the survival of the 2D topological phase.

To mimic the bulk stacking fault of Te-Te type, we construct the $n[\text{I-Bi-Te}]_{\text{TL}}-[\text{I-Bi-Te-Te-Bi-I}]_{\text{SL}}-n[\text{Te-Bi-I}]_{\text{TL}}$ structure with $n = 8$. The outer, iodine-terminated, surfaces of the film as before were passivated by hydrogen. As seen in Fig. 6(c) the SL localized states lie within the BiTeI bulk gap and the principal difference of the spectrum from that shown in Fig. 5 is absence of the Rashba splitting of these states. The SL gap, which remains inverted, has the width of 59.5 meV that is

FIG. 5. Layer- (a) and spin-resolved (b) spectrum for $\text{Bi}_2\text{Te}_2\text{I}_2\text{-SL@BiTeI}$ structure. (c) Orbital-resolved band structure in the vicinity of the Γ gap.

almost the same value as in the case of the free-standing $\text{Bi}_2\text{Te}_2\text{I}_2$ SL. Thus, like in case of the SL@BiTeI, the 2D TI phase survives being built into the BiTeI bulk and hence the Te-Te bulk stacking fault can be considered as 2D topological defect.

D. Search for 2D and 3D topological phases in $\text{Bi}_2\text{Te}_2\text{Br}_2$ and $\text{Bi}_2\text{Te}_2\text{Cl}_2$

Finally, we consider 2D and 3D centrosymmetric phases constructed from TLs of the related band insulators BiTeBr

and BiTeCl. Despite the bulk stacking faults, which is a key element for centrosymmetric BiTeX phases, missing in BiTeBr and BiTeCl obtained by the Bridgeman method as follows from the experiment [31] demonstrating the absence of the mixed-terminated surfaces in these materials, however, one can assume that centrosymmetric films of BiTeBr and BiTeCl can, in principle, be epitaxially grown.

Calculating the total energies of free-standing SLs of $\text{Bi}_2\text{Te}_2\text{Br}_2$ and $\text{Bi}_2\text{Te}_2\text{Cl}_2$ we found that they have lower (by 98 and 91 meV, respectively) energy compared to that

FIG. 6. (a) Spectrum of the centrosymmetric I-Bi-Te-SL-Te-Bi-I structure with layer localization. (b) In-plane spin components projected onto the upper half of the TL'-SL-TL structure. (c) Spectrum for inversely stacked BiTeI thick films with $\text{Bi}_2\text{Te}_2\text{I}_2\text{-SL}$ in the middle.

FIG. 7. Band spectra of free-standing $\text{Bi}_2\text{Te}_2\text{Br}_2$ (a) and $\text{Bi}_2\text{Te}_2\text{Cl}_2$ (b) SLs. The dependence of the $\bar{\Gamma}$ -gap width on the number of SLs in $\text{Bi}_2\text{Te}_2\text{Br}_2$ and $\text{Bi}_2\text{Te}_2\text{Cl}_2$ thin films (c). The sign of the gap is positive for topologically trivial film and negative for nontrivial one. (d) Surface electronic structure of the 3D TI $\text{Bi}_2\text{Te}_2\text{Br}_2$.

of the BiTeBr and BiTeCl double TLs. These values are comparable with the energy gain for $\text{Bi}_2\text{Te}_2\text{I}_2$ SL with respect to BiTeI double TLs which amounts to 88 meV. However, if the energy difference between bulk BiTeI and $\text{Bi}_2\text{Te}_2\text{I}_2$ phases is only 0.5 meV, while the bulk phases composed of $\text{Bi}_2\text{Te}_2\text{Br}_2$ and $\text{Bi}_2\text{Te}_2\text{Cl}_2$ SLs are less favorable in comparison with the corresponding BiTeBr and BiTeCl noncentrosymmetric bulk crystals. The energy loss for $\text{Bi}_2\text{Te}_2\text{Br}_2$ with respect to BiTeBr is 20.75 meV per BiTeBr f.u. and 26.35 meV/f.u. for the $\text{Bi}_2\text{Te}_2\text{Cl}_2$ system as compared with BiTeCl .

The band spectra of $\text{Bi}_2\text{Te}_2\text{Br}_2$ and $\text{Bi}_2\text{Te}_2\text{Cl}_2$ single, free-standing SLs [Figs. 7(a) and 7(b)], in general, are similar to that of $\text{Bi}_2\text{Te}_2\text{I}_2$; however, they have larger band gaps, 106 and 203 meV, respectively, and, according to $\mathbb{Z}_2$ calculations, these centrosymmetric $\text{Bi}_2\text{Te}_2\text{Br}_2$ and $\text{Bi}_2\text{Te}_2\text{Cl}_2$ SLs are topologically trivial.

Next, like the case of $\text{Bi}_2\text{Te}_2\text{I}_2$, we addressed the electronic structure of the $\text{Bi}_2\text{Te}_2\text{Br}_2$ and $\text{Bi}_2\text{Te}_2\text{Cl}_2$ bulk. We revealed that $\text{Bi}_2\text{Te}_2\text{Br}_2$ has an inverted band gap of 62 meV, while $\text{Bi}_2\text{Te}_2\text{Cl}_2$ bulk is a trivial band insulator with the gap of 92.5 meV and thus it is trivial in both 2D and 3D phases.

Considering the dependence of the $\bar{\Gamma}$ gap and the topological invariant on the film thickness for $\text{Bi}_2\text{Te}_2\text{Br}_2$ and $\text{Bi}_2\text{Te}_2\text{Cl}_2$ [Fig. 7(c)], we found that in contrast to $\text{Bi}_2\text{Te}_2\text{I}_2$ where along with a sharp decrease in the value of the gap, the oscillating

behavior of $\mathbb{Z}_2$ with the number of SLs was obtained [14], the $\text{Bi}_2\text{Te}_2\text{Cl}_2$ demonstrates a smooth decrease in the gap to its bulk value, being the trivial insulator at any film thickness, while $\text{Bi}_2\text{Te}_2\text{Br}_2$ at the five-SL thickness becomes a 2D TI with the small inverted gap of 6 meV. For thicker films, the gap is zero, which indicates the converged Dirac cone of the 3D TI phase. The surface spectrum of the latter is shown in Fig. 7(d).

IV. CONCLUSIONS

In summary, by using first-principles calculations we have examined the topologically protected edge states and topologically trivial Rashba-split spin-polarized dangling bond states that emerged at the different edges of the 2D topological insulator $\text{Bi}_2\text{Te}_2\text{I}_2$ of one-sextuple-layer thickness. We have revealed that irrespective of the edge plane the dangling bond states lie rather far from the 2D band projected gap energy region, where the $\bar{\Gamma}$ Dirac state resides. We also suggested the appropriate substrate for 2D $\text{Bi}_2\text{Te}_2\text{I}_2$ QSHI, which is a parental noncentrosymmetric BiTeI compound. This substrate guarantees the absence of both lattice mismatch and interface charge transfer effects. Since BiTeI is the material with giant Rashba-type spin splitting, it produces a sizable spin splitting in the 2D band structure of QSHI films. However, despite the Rashba splitting in the states forming the gap the latter remains inverted and the 2D topological phase survives in the $\text{Bi}_2\text{Te}_2\text{I}_2/\text{BiTeI}$ heterostructure as confirmed by the $\mathbb{Z}_2$ index calculation. It is remarkable that the 2D TI phase of $\text{Bi}_2\text{Te}_2\text{I}_2$ also survives in the bulk BiTeI , where the $\text{Bi}_2\text{Te}_2\text{I}_2$ -SL might exist as two inversely faced TLs forming a Te-Te stacking fault. We have also systematically examined the possibility of realizing nontrivial 2D and 3D topological phases in thin films and bulk crystals of related hypothetical compounds composed of centrosymmetric sextuple layers of BiTeBr and BiTeCl . We have revealed that ultrathin centrosymmetric films of $\text{Bi}_2\text{Te}_2\text{Br}_2$ are trivial band insulators up to five-SL thickness, and in the 3D limit $\text{Bi}_2\text{Te}_2\text{Br}_2$ is a strong TI, while both 2D and 3D phases of $\text{Bi}_2\text{Te}_2\text{Cl}_2$ are topologically trivial. We hope that our study will motivate further experimental works on topologically nontrivial centrosymmetric BiTeX systems.

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