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Quantum spin Hall insulators in chemically functionalized As (110) and Sb (110) films*

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We propose a new type of quantum spin Hall (QSH) insulator in chemically functionalized As (110) and Sb (110) film. According to first-principles calculations, we find that metallic As (110) and Sb (110) films become QSH insulators after being chemically functionalized by hydrogen (H) or halogen (Cl and Br) atoms. The energy gaps of the functionalized films range from 0.121 eV to 0.304 eV, which are sufficiently large for practical applications at room temperature. The energy gaps originate from the spin–orbit coupling (SOC). The energy gap increases linearly with the increase of the SOC strength λ/λ_0. The Z_2 invariant and the penetration depth of the edge states are also calculated and studied for the functionalized films.

Keywords: quantum spin Hall insulators, density functional theory (DFT), chemical functionalization, As (110) and Sb (110) film, Z_2 topological invariants

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1. Introduction

Topological insulators (TIs) have attracted attention due to their potential applications in spintronics and topological quantum computation.[1–3] These materials are insulating in the bulk but they are metallic on their surface or edge, where spin and momentum are perpendicularly locked, and their topological nontrivial electronic structure is protected by time reversal symmetry. Compared with the surface state of three-dimensional (3D) TI, the edge state of two-dimensional (2D) TIs is more robust against backscattering because electrons can only propagate along two directions in the edge state of 2D TI. The two-dimensional TI is also named quantum spin Hall (QSH) insulator. Kane and Mele proposed that graphene is a QSH insulator,[4–6] in which the spin–orbit coupling (SOC) opens a band gap at the Dirac point.[7] However, Yao *et al.* show that it is almost impossible to observe the QSH effect of graphene at a finite temperature due to the very small energy gap.[8] So far there have only been a few systems which have experimentally been shown to be QSH insulators, such as HgTe/CdTe,[9,10] InAs/GaSb quantum wells,[11,12] and Bi (111) film.[13] Recently, the QSH effect at temperature up to 100 K was observed in WTe_2 monolayers.[14] In order to detect and utilize the QSH effect at room temperature, the bulk gap of QSH insulators must be large enough to suppress the thermal perturbation of activated carriers. Chemical functionalization is an effective method to design new QSH insulators that have the large gaps,[15] such as chemically functionalized tin films.[16] Previous studies on QSH insulators mainly focused on honeycomb-lattice related materials.[13,17–20] The ultrathin tin film in the buckled honeycomb lattice is predicted to be a QSH insulator with a 0.1-eV bulk gap. When decorated with halogen atoms, this gap can be further enlarged to 0.3 eV.[16] After functionalization, GaAs,[22] GaBi,[23] and stanene are reported to be quantum spin Hall insulators.[24] The Pb film of buckled honeycomb structure is predicted to be a class of new 2D TIs when decorated with halogen atoms.[25] Recently, a Bi film in an octagonal tiling (OT) structure is predicted to have a bulk gap of 0.33 eV, which is the largest energy gap in the bulk gaps of reported elemental 2D TIs.[26] Moreover, the chemically functionalized Bi (110) films are transformed into QSH insulators and maintain the topologically nontrivial properties against large strains and substrate interaction.[27] The 2D TIs have a lot of potential applications in fabricating new quantum devices due to dissipationless spin and charge current. In this work, metallic As (110) and Sb (110) films are chemically functionalized by using hydrogen (H) or halogen (Cl and Br) atoms. The calculation of phonon spectra shows that these functionalized films are dynamically stable. First-principles electronic structure calculations show that the energy gap for each of these functionalized films is opened due to the strong spin–orbit coupling. Chemical functionalization is a powerful tool to stabilize the 2D structure and enlarge the band gap for As (110) and Sb (110) film. The Z_2 invariant further shows that these functionalized films have topologically nontrivial properties. The

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energy gaps of these functionalized films range from 0.121 eV to 0.304 eV, which are sufficiently large for practical applications at room temperature. The topological edge states are also investigated.

2. Computational methods

The calculations are carried out within the framework of density functional theory (DFT) and the generalized gradient approximations (GGA) with the Perdew–Burke–Ernzerhof (PBE)[28] type functional as implemented in the Vienna *ab initio* simulation package (VASP).[29–31] The SOC calculations are based on relativistic spin-density functional theory supported by the non-collinear mode of VASP. A vacuum layer of 20 Å is added into the cell in the calculations of the films. Phonon dispersions are calculated with the help of a phonopy package[32] in $5\times5\times5$ and $7\times7\times7$ supercells respectively. The atoms are relaxed until the residual forces are less than 0.01 eV/Å. An $18\times18\times1$ k-mesh is used for both the geometry optimization and the self-consistent calculations.

3. Results and discussion

3.1. Atomic structures and dynamical stability

Figure 1(a) shows the crystal structure of bulk X (X = As, Sb). The X atoms in the (110) plane are marked within the blue cuboid. The layer of X (110) is sheared from bulk X along the (110) plane. The atomic geometry of functionalized X (110) film is shown in Fig. 1(b). The unit cell is rectangular, and it contains two X (X = As, Sb) atoms and two D (D = H, Cl, Br) atoms. The inversion center is marked by a red solid circle in the unit cell of X–D. These X–D films have a simple orthorhombic crystal structure with the space group C_{2h}. The heights of these two X atoms differ by a small amount (Δh). During functionalization, one X atom is decorated by an H or halogen (Cl and Br) atom on the top side and the other X atom is decorated on the bottom side. In that case, the inversion symmetry is maintained. The relaxed lattice constants (a, b), the buckling distance Δh, and the energy gaps of X–D (X = As, Sb and D = H, Cl, Br) films are listed in Table 1. Lattice constants of Sb–D (D = H, Cl, Br) are larger than those of As–D since Sb has a larger atomic radius. Similarly, lattice constants of X–Br (X = As, Sb) are larger than those of X–Cl and lattice constants of X–Cl (X = As, Sb) are larger than those of X–H, because the atomic radius of the halogen element increases with the increase of atomic number.

The definition of formation energy is

$$E_{\text{formation}} = E_{X-D} - E_X - E_{D_2},$$

where E_{X-D}, E_X, and E_{D_2} denote the total energy of X–D film in one unit cell, X in one unit cell and D_2, respectively. The formation energies of X–D films are all negative, which shows the stability of the X–D film. The formation energies of all X–D films are listed in Table 1. The phonon dispersion of all X–D (X = As, Sb and D = H, Cl, Br) films are calculated and no imaginary modes are found. It indicates that these functionalized X–D films are dynamically stable. Figure 1(c) shows the phonon spectra of As–Cl, where all the modes are positive at the whole K points. There are twelve phonon bands in Fig. 1(c), consistent with the degree of freedom of the system.

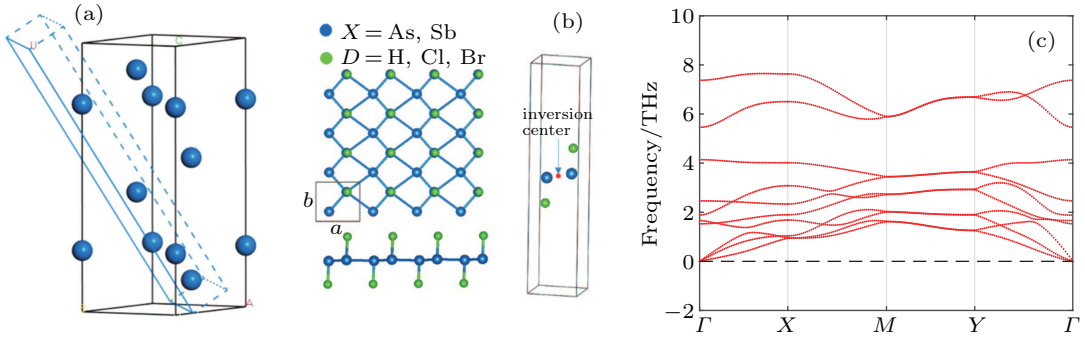


Fig. 1. (color online) (a) Hexagonal unit cell of bulk X (X = As, Sb) and the X atoms in the (110) plane marked within the blue cuboid. (b) Diagram of the decorated X–D (D = H, Cl, Br) structure from top view and side view respectively. The inversion center is marked in the red point in the unit cell of X–D. Blue represents X atoms and green refers to D atoms. (c) Phonon bands of As–Cl film.

Table 1. Lattice constants (a, b) of unit cell, height difference (Δh) of X (X = As, Sb) atoms in the unit cell, energy gaps of X–D with SOC, and formation energy of X–D.

System (X–D)	As–H	As–Cl	As–Br	Sb–H	Sb–Cl	Sb–Br
a/Å	4.2316	4.3104	4.3155	4.5896	4.6055	4.6452
b/Å	3.8106	3.8509	3.8909	4.3766	4.3671	4.3696
Δh/Å	0.0041	0.0865	0.1048	–0.0257	–0.0734	–0.0614
gap(soc)/eV	0.1724	0.1208	0.1406	0.3044	0.2859	0.2885
$E_{\text{formation}}$/eV	–0.6215	–2.6506	–2.2366	–0.2799	–3.0514	–2.6951

3.2. Electronic structures

The band structures of these X–D films are calculated with and without considering spin–orbit coupling (SOC) respectively. In order to calculate the electronic structure of X–D film, we add one vacuum layer of 20 Å into the unit cell, which is large enough to eliminate the interaction between 2D layers. Though freestanding As (110) and Sb (110) films are metallic, the functionalized X–D films are all insulating. Listed in Table 1 are the energy gaps of these X–D films with SOC. The energy gaps with SOC range from 0.121 eV to 0.304 eV. The energy gaps of Sb–D are larger than those of As–D. The Sb atom is heavier than the As atom, which makes the SOC of Sb–D stronger than that of As–D. The energy bands of As–Cl and Sb–Cl are shown in Fig. 2. When the SOC is not considered, their valence band and the conduction band touch around the X point. The calculated energy gap without SOC is precisely 0 eV in all cases. After SOC is taken into account, energy gaps are opened. The energy gap of As–Cl and Sb–Cl are 0.121 eV and 0.286 eV respectively when the effect of SOC is included.

In order to investigate the relationship between energy gap and the SOC strength, we change the SOC strength ratio λ/λ_0 to tune the SOC strength. λ and λ_0 represent the tuned SOC strength and the natural SOC strength respectively. The Dirac cone will be opened when the SOC strength is tuned from 0 to λ_0. In the process of tuning the SOC strength, X–D films maintain their topological properties. As the SOC strength λ/λ_0 increases, the energy gap increases linearly as shown in Fig. 4(a).

We make the diagrams of orbital projection as shown in Fig. 2. All these X–D films show similar behaviors. At the Dirac point, the main contribution originates from P_x without SOC. When calculating band structures with SOC, we find that the energy gaps are opened. The SOC-induced gap opening is a common mechanism of TIs. Therefore, it strongly implies that these films are QSH insulators.

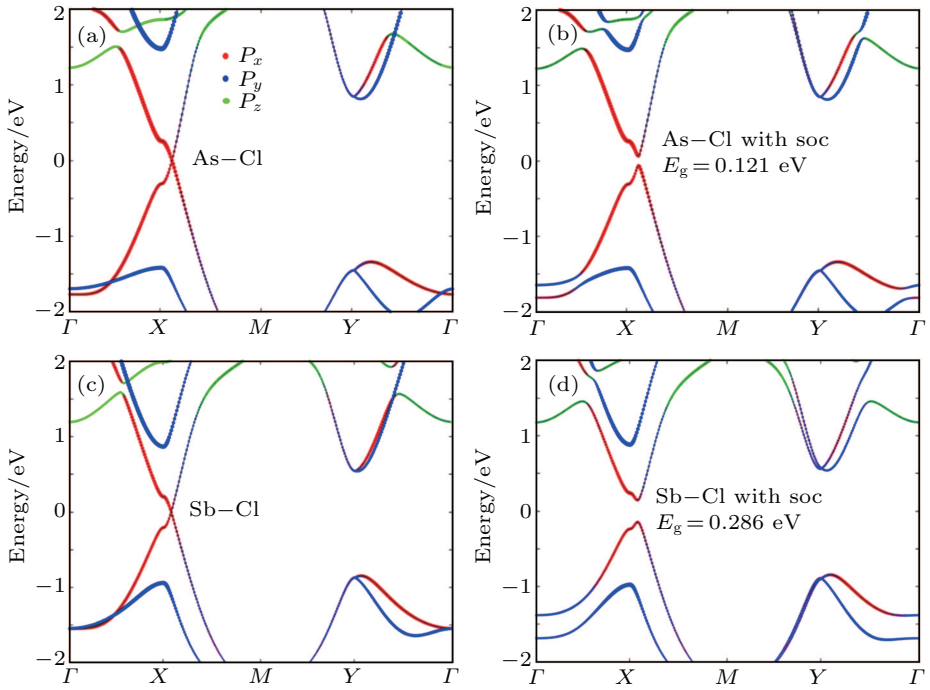


Fig. 2. (color online) (a) Energy band of As–Cl without SOC. (b) Energy band of As–Cl with SOC. (c) Energy band of Sb–Cl without SOC. (d) Energy band of Sb–Cl with SOC. The size of red points, blue points, and green points represent the contribution of P_x, P_y, and P_z of X (X = As, Sb) respectively.

3.3. Topological edge states

Nanoribbons of these X–D films are constructed and the edge states are observed in all these X–D films. The width of nanoribbon is large enough to eliminate interaction between the two edges. The band structures and the atomic geometry of As–Cl ribbon are shown in Fig. 3. The gapless edge states connect the valence band with the conduction band, and the Dirac point is located at the Γ point. The Dirac states at the Γ point mainly originate from the $P_{x,y}$ orbitals of X edge atoms. The size of red solid circle represents the contribution of X edge atoms within two unit cells from the two edges.

We make the real space projections of wave functions of Dirac states at the Γ point for all types of X–D films. The results for As–Cl are shown in Fig. 3(b), which indicates that the edge states mainly appear within two unit cells from the two edges. The edge states mainly origin from edge atoms and have a small penetration depth of 1 nm approximately. This feature is consistent with the band structures of the ribbon discussed above. The red solid circles that represent the X atomic contribution of two unit cells from the two edges only appear on the edge states.

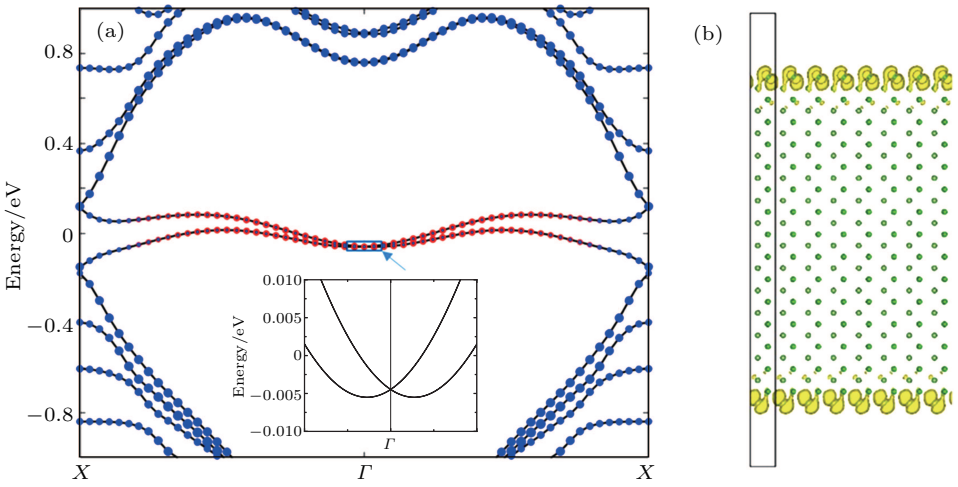


Fig. 3. (color online) (a) Band structure of nanoribbon of As–Cl. Size of red solid circle represents the contribution of X edge atoms within two unit cells from two edges. Size of blue solid circle represents the contribution of interior atoms. Symbol size indicates the contribution weight. Inset shows a magnified part of the edge states around the Γ point. (b) Diagram of nanoribbon and the real space projection of wave functions at the Γ point.

3.4. The Z_2 topological invariants

In order to confirm these X–D insulators that are indeed for 2D topological insulators, we calculate the Z_2 topological invariant (ν), which is used to describe the topological property of the time-reversal-symmetry system.[33–35] When the system has an inversion symmetry, the calculating process of the Z_2 topological invariants (ν) could be simplified dramatically. The arithmetic product of the wave functions parities at the four time-reversal-invariant moment (TRIM) points is used to determine the Z_2 number of these X–D films. In a 2D system, $\nu = 1$ corresponds to a nontrivial insulator and $\nu = 0$ corresponds to a trivial insulator. ν has the relations as follows:

$$\delta_i = \prod_{m=1}^{N} \xi_{2m}(\Gamma_i), (-1)^{\nu} = \prod_i \delta_i,$$

where δ_i is the product of the parity eigenvalues at the four time-reversal-invariant (TRIM) points, Γ_i represents the four TRIM points when $i = 1, 2, 3, 4$, ξ_{2m} is the parity eigenvalue of wave function, and N is the total number of occupied bands.

Table 2. Values of total parity (δ) at the four time-reversal-invariant-moment (TRIM) points and the Z_2 topological invariant (ν).

System (X–D)	As–H	As–Cl	As–Br	Sb–H	Sb–Cl	Sb–Br
$\delta(\Gamma)$	+	−	-	+	−	−
$\delta(X)$	−	+	+	−	+	+
$\delta(Y)$	−	+	+	−	+	+
$\delta(M)$	−	+	+	−	+	+
ν	1	1	1	1	1	1

In all these X–D films, the sign of δ at the Γ point is different from those at other TRIM points (X, Y, M). Specifically, the sign of δ at the Γ point is positive for H-functionalized X–H (As–H, Sb–H). However, the sign of δ at the Γ point is negative for other halogen atom decorated X–D (X–Cl, X–Br). The values of the product of parity eigenvalue and the Z_2 topological invariant (ν) are listed in Table 2. The values of Z_2 topological invariant (ν) are 1 in all these cases of X–D (X = As, Sb, D = H, Cl, Br), which confirms that all these X–D films are nontrivial insulators.

3.5. Energy gap as a function of strain

The topological phase is robust against nonmagnetic perturbations, such as strain. We exert a uniform in-plane strain on these X–D films and calculate their band structure. It is convenient to use $\varepsilon = (a_s - a_0)/a_0$ to define the magnitude of the strain, where the a_0 represents the optimized lattice constants (a, b) and a_s denotes the new lattice constant with strain. We optimize the atomic positions within the unit cell for the constants (a, b) of each fixed lattice. The magnitude of the strain (ε) for X–D film ranges from -7% to 11%. The relationship between energy gap and strain is plotted in Fig. 4(b). We find that the energy gap of Sb–Cl is larger than the As–Cl no matter how large the magnitude of the stain is. The energy gap also becomes smaller slightly with increasing tensile strain. Under compressive strain, the gap becomes slightly larger than under tensile strain. The overall change in the energy gap is relatively small. Considering the linear relation between the gap and the SOC strength, we conclude that the gap originates from the SOC strength and the strain has very small influence on the energy gap.

The band structures of As–Cl for the strains of -7%, 0%, and 11% are shown in Fig. 5. The band gaps under these three strains (-7%, 0%, 11%) are almost the same. As the strain increases, the energy bands become less dispersive. The overall difference among three band structures is small. The results of band structure calculations show that the energy gaps originate from the spin–orbit coupling (SOC). These properties make it easier to realize quantum spin Hall insulator experimentally because the topological phase transition does not occur when we exert an external strain (-7% to 11%) on these X–D films.

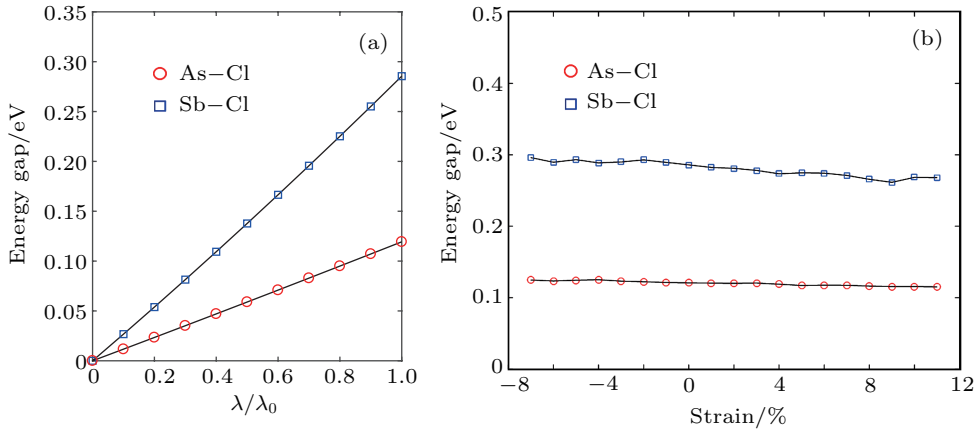


Fig. 4. (color online) (a) Plots of energy gap versus SOC strength ratio (λ/λ_0), with λ and λ_0 representing the tuned SOC strength and the natural SOC strength respectively. (b) Plots of energy gap of As–Cl and Sb–Cl with SOC versus in-plane strain. Red empty circle and blue empty square represent As–Cl and Sb–Cl respectively.

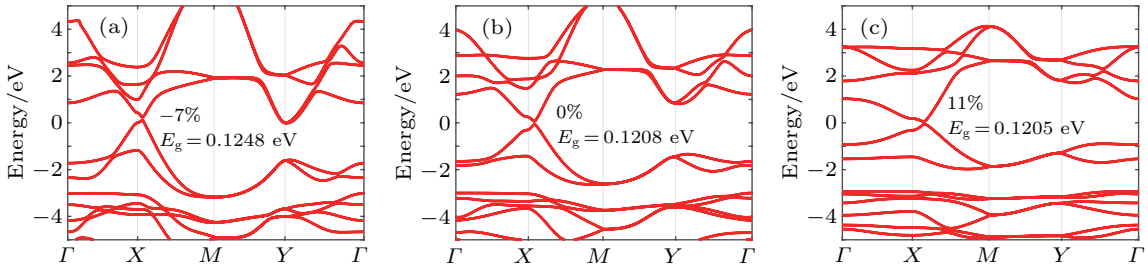


Fig. 5. (color online) Band structures of As–Cl when the strain is tuned to (a) −7% (b) 0%, and (c) 11%, respectively.

4. Conclusions

A new type of quantum spin Hall insulator *X*–*D* (*X* = As, Sb and *D* = H, Cl, Br) is predicted by using the first-principles method. Phonon spectra indicate that these *X*–*D* films are dynamically stable. Their energy gaps with SOC range from 0.121 eV to 0.304 eV, sufficiently large for practical applications at room temperature. The penetration depths of the edge state of all these *X*–*D* films are about 1 nm, and their Z_2 topological invariant is also calculated, which confirms that these *X*–*D* films are quantum spin Hall insulators.

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