Robust large-gap quantum spin Hall insulators in chemically decorated arsenene films

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Abstract

Based on first-principles calculations, we propose one new category of two-dimensional topological insulators (2D TIs) in chemically functionalized (-CH3 and -OH) arsenene films. The results show that the surface decorated arsenene (AsCH3 and AsOH) films are intrinsic 2D TIs with sizeable bulk gap. The bulk energy gaps are 0.184 eV, and 0.304 eV in AsCH3 and AsOH films, respectively. Such large bulk gaps make them suitable to realize quantum spin Hall effect in an experimentally accessible temperature regime. Topologically helical edge states in these systems are desirable for dissipationless transport. Moreover, we find that the topological properties in these systems are robust against mechanical deformation by exerting biaxial strain. These novel 2D TIs with large bulk gaps are potential candidate in future electronic devices with ultralow dissipation.

Introduction

Two-dimensional topological insulators (2D TIs) [1–8] have attracted great research enthusiasm due to their exotic topological properties. Such states are characterized by an insulating bulk and gapless edge states in which the electrons with different spin polarizations propagate in opposite direction. These gapless edge states are topologically protected against backscattering by time-reversal symmetry, making them quite promising for the realization of conducting channels without dissipation. Quantum spin Hall (QSH) edge states have been experimentally demonstrated in very few materials so far, including HgTe/CdTe [5, 6] and InAs/GaSb [7, 8] quantum wells. However, these quantum wells have serious limitations such as difficulty in processing and small band gaps of displaying QSH effect. Therefore, searching easily accessible systems exhibiting QSH effect with large bulk gaps will be a major scientific endeavor.

Since the graphene was mechanically exfoliated [9], vigorous investigation of graphene-like 2D materials consisting of single element has been fueled, such as silicene [10–12], germanene [13], stanene [14], phosphorene [15, 16], Sb [17, 18] and Bi films [19–21]. Among these 2D materials, some have been theoretically predicted to be potential candidates for realization of QSH effect [22–27]. In addition, we notice that in 2D systems associated with group IV and V elements, the investigation of layered arsenic (As) has been largely overlooked, although the bulk arsenic has been extensively studied. The three arsenic allotropes are metallic gray, yellow, and black arsenic, among which gray arsenic is the most common and stable form. Gray arsenic (α-As) adopts a stacking structure of warped graphene-like layers and the interlayer interaction is dominated by van der Waals force. Because of weak bonding between the layers, gray arsenic is so brittle that layered arsenic can be produced through mechanical cleavage and exfoliation from bulk form as in the case of graphene and phosphorene. Very recently, arsenene, 2D graphene analog of arsenic, is proposed to be a semiconductor with promising electronic and optoelectronic properties, which paves the way for applications in transistors, mechanical sensors and optoelectronic devices [28–31]. However, the topological properties (trivial or nontrivial) of arsenene are studied rarely [32–34]. Although the topological phase transition from trivial to nontrivial phase can be triggered by stretched strain (larger than 11%), such large strain, particularly biaxial
tensile strain, is very challenging to implement for 2D materials. Therefore, other effective and feasible routes should be proposed, such as surface decoration.

Motivated by recent studies on arsenene, we investigate electronic and topological properties of free-standing arsenene and chemically decorated (-CH$_3$ and -OH) arsenene layers by density functional theory calculations. We found that the pure arsenene can be driven into QSH insulators by surface decoration with -CH$_3$ and -OH groups. Importantly, the sizable bulk gaps in these two systems can reach up to 0.184 eV and 0.304 eV, respectively, which is suitable to realized QSH effect at room temperature. In addition, the nontrivial topology in both systems is robust against external strain. The robust large-gap 2D TIs systems are quite promising for applications in spintronics.

**Computational details**

First-principles calculations based on density functional theory were performed by the Vienna *ab initio* simulation package [35]. The Perdew–Burke–Ernzerhof [36] generalized gradient approximation was used to describe the exchange-correlation potential. The kinetic energy cutoff is 500 eV and the convergence threshold for energy is $10^{-6}$ eV. The lattice constants and the atom coordinates were fully optimized until the forces on each atom is less than $10^{-3}$ eV Å$^{-1}$. The Brillouin zone integration is performed with a $17 \times 17 \times 1$ $k$-mesh for geometry optimization and self-consistent calculations. To simulate isolated thin films, a sufficiently large vacuum space of 20 Å is used to rule out any interactions between the neighboring films. The SOC is included in self-consistent electronic structure calculations. The phonon dispersions are calculated by density functional perturbation theory using Quantum ESPRESSO [37].

**Results and discussion**

Among three possible allotropes including puckered, buckled and planar structures, the buckled arsenene possesses the most stable configuration [28, 30]. Therefore, our attention will focus on the structural and electronic properties of buckled configuration in the following section. The geometric structure of buckled arsenene is shown in figure 1(a). Through the structural relaxation, the structural parameters are calculated as listed in table 1, which are in good agreement with previous works. The calculations of both phonon band dispersion and cohesive energy suggest arsenene is dynamically stable with cohesive energy of $-2.96$ eV/atom, which is defined as $E_b = E_{\text{tot}}/N - E_{\text{As}}$, where $E_{\text{tot}}$ is the total energy of arsenene, $N$ is the number of As atom, and $E_{\text{As}}$ is the energy of single As atom.

![Figure 1.](image-url)
Then the band structure of arsenene with SOC is calculated as shown in figure 1 (b). Compared with the case without SOC, the degenerate bands near Fermi level are lifted out. The band gap reduces to the value of 1.48 eV, which is slightly decreased than that without SOC (1.61 eV), but it is still indirect, suggesting that the intrinsic SOC of As atoms has a very little impact on the electronic properties in itself. With the orbital projections on each band in figure 1 (b), there is no significant change observed with respect to those without SOC, where the contribution mainly comes from the \textit{p}$_x$, \textit{p}$_y$, and \textit{p}$_z$ orbitals of As atoms. Because the SOC strength of As atoms is very weak relative to large energy gap (∼1.61 eV), it is obvious that arsenene is trivial in topology.

Previous works have reported that biaxial tensile strain can induce topological phase transition from trivial to nontrivial for arsenene [33, 34]. However, the required strain is beyond 11%, which is challenging and not flexible to implement for current technology. Hence effective and feasible method should be proposed for arsenene. Many reports have shown that chemical decoration is helpful to modulate the structural, electronic and topological properties of 2D materials, such as chemically modified germanene [38], stanene [22], and Bi film [39–42]. It has been recently shown to be also effective in arsenene to induce nontrivial phase with full hydrogenation and halogenation [32]. Very recently, we notice that the methyl-substituted germanene (GeH), GeCH$_3$ film, has been well produced [43] in the experiment. The GeCH$_3$ film has considerably enhanced thermal stability up to 250 °C superior to GeH film. Recent theoretical work has pointed out that the GeCH$_3$ film is a trivial insulator, which becomes a QSH insulator under a large tensile strain [44]. Similarly, methyl-substituted arsenene (AsCH$_3$) film may be synthesized using the analogous method. A question in our mind is: would the AsCH$_3$ film be a QSH insulator without strain effect?

The equilibrium structure of arsenene film terminated by methyl is presented in figure 2(a), which shares a similar geometric structure as AsH. The -CH$_3$ group are bonded to the As atoms on both sides of arsenene in an alternating manner. There are two As atoms and two -CH$_3$ groups per unit cell. The detailed parameters of optimized structure, including lattice constant, As–As bond length, As–C bond length and buckling height, can be seen in table 1. The lattice constant has been largely expanded by chemical modification of methyl, compared with that of pure arsenene, while the buckling height is greatly decreased to 0.12 Å from 1.40 Å due to the chemical bonding between methyl and As atoms. If AsCH$_3$ film is stable, it may be one of good candidates to realize QSH effect. To confirm this point, the phonon dispersion thus is calculated. As shown in figure 2(b), only minor negative frequencies appear in the vicinity of the Γ point, which are well known artifacts of the numeric. Therefore, AsCH$_3$ is dynamically stable.

Figure 2. (a) Atomic structures and (b) corresponding phonon spectrum of AsCH$_3$ film. (c) Atomic structures and (d) corresponding phonon spectrum of AsOH film.
Except \(-\text{CH}_3\) group, hydroxyl \((-\text{OH})\) adsorption may be also realized on arsenene film, particularly when the alloyed Ge\(_{1-x}\)Sn\(_x\)H\(_{1-x}\)(OH)\(_x\) has been recently synthesized in the experiment [45, 46]. In this 2D alloy, the Ge atom is terminated with H while Sn atom is terminated with \(-\text{OH}\) group, indicating \(-\text{OH}\) adsorption may be available in 2D arsenene film. The schematic structure of AsOH film is shown in figure 2(c) after performing the full optimization of atomic positions. The lattice parameters of equilibrium structure are listed in table 1. We find that the O atoms are right on the top and bottom of As atoms, while the bond angle between As–O and O–H bonds is \(~109.3^\circ\). The lattice constant is 4.59 Å, which is larger than that of pure arsenene but less than that of AsCH\(_3\) film. The buckling height is 0.052 Å, a nearly quasi-planar structure, and the bond length between As and O atom is less than that between As and C atom, indicating stronger interaction between hydroxyl and As atoms.

To confirm its stability, the calculation of the phonon dispersion is also performed. As shown in figure 2(d), minor negative frequencies also emerge as in the case of AsCH\(_3\), which can be ignored, suggesting that it is dynamically stable.

The band structures of AsCH\(_3\) and AsOH films are calculated as shown in figure 3. One can clearly see in figure 3(a) that the bands are reshaped by chemical decoration with both conduction band minimum (CBM) and valence band maximum (VBM) located at the \(K\) point, compared with those of pure arsenene. When the SOC is taken into consideration, a direct energy gap is opened up at the Dirac point. The size of energy gap is 0.184 eV, which is slightly less than that of GeCH\(_3\) \((~0.193\) eV\) at the \(\Gamma\) point. By projecting different orbitals onto the bands, the bands near CBM and VBM at the \(\Gamma\) and \(K\) point are dominated by \(p_x\) and \(p_y\) states of As atoms, which is significantly different from those of GeCH\(_3\) with the s states occupying CBM and p states occupying VBM [44]. The band structure of AsOH with SOC is presented in figure 3(b). The energy gap in AsOH film is larger than those of AsH and AsCH\(_3\), which can reach up to 0.304 eV comparable to that of iodinated stanene. The bands around the Fermi level at the \(K\) point in AsOH are mainly contributed by \(p_x\) and \(p_y\) orbitals of As and O atoms, leading to strong \(p_{xy}\) orbital hybridization. The increasing of energy gap in AsCH\(_3\), AsH and AsOH film is in close correlation with the electronegativity increasing from -CH\(_3\) to -H to -OH. Compared with pure arsenene, the \(p_y\) orbital components are removed from the low-energy spectrum in the decorated arsenene with dangling bonds saturated. The role of SOC in AsCH\(_3\) and AsOH films is to open up energy gap at the \(K\) point as in the case of surface decorated Bi and Sb [39, 41], suggesting that the AsCH\(_3\) and AsOH films may be 2D TIs.

One effective way to distinguish nontrivial TIs from trivial insulators is to calculate the topological invariant \(Z_2\) [47]. For the 2D TI phase, the topological invariant is calculated from the parities of the Bloch wave functions for occupied bands at time-reversal invariant momenta points, one \(\Gamma\) and three \(M\) points, as

\[
\delta_\ell = \prod_{m=1}^{N} \xi_{2m}^\ell (K_i), \quad (-1)^\nu = \prod_{i=1}^{4} \delta_i = \delta (\Gamma) \delta_3 (M),
\]

where \(\xi_{2m} = \pm 1\) denotes parity eigenvalues and \(N\) is the number of the occupied bands. \(\nu = 1\) indicates a nontrivial phase. To determine the topology of AsCH\(_3\) and AsOH, the respective topological invariants \(Z_2\) are calculated. The parities at the \(\Gamma\) and \(M\) points as well as the total values \(Z_2\) are listed in table 1. The \(Z_2\) number equals 1 for both AsCH\(_3\) and AsOH films, while it is zero for pure arsenene, suggesting that topological phase transition from trivial to nontrivial phase emerges. Due to the nontrivial topology in AsCH\(_3\) and AsOH, they are robust against back-scattering, which is important for the applications in ultralow-dissipation devices. Hence, chemical decoration is further revealed not only to regulate the electronic structure but also to regulate the topological properties of arsenene. It is worthwhile to point out that the SOC-induced energy gaps in AsCH\(_3\) and AsOH are rather larger than the thermal energy \(k_B T (~26\) meV\) at room
temperature [44], meaning that QSH effect can be experimentally observed and potential for applications at room temperature.

The existence of helical gapless edge states is one of the prominent features of 2D TIs. To see the nontrivial topological nature, the calculations of edge states hence are performed with cut 2D film into 1D nanoribbon. The armchair nanoribbon structure with symmetric edges is chosen for both AsCH₃ and AsOH. The width of nanoribbon is large enough to sufficiently avoid the interaction between two edges. The calculated edge states of AsCH₃ and AsOH are shown in figures 4(a) and (b), where the edge states are denoted by red lines. One can clearly see that the valence and conduction bands are connected through the edge states. Interestingly, such edge states cross linearly exactly at Fermi level at the Γ point, in which charge carriers can be regarded as massless Dirac fermions. We also find that the cross point is very similar to that of graphene with the slope, namely the first derivatives of band energies near the Fermi level, unchanged, showing typical Dirac property. The Fermi velocity $v_F$ of helical edge states of AsCH₃ and AsOH is in the magnitude of $10^5$ m s$^{-1}$. The edge states are energetically degenerated due to symmetric edges, which are located at different boundaries, respectively. The helical edge states further confirm the topologically nontrivial nature of AsCH₃ and AsOH films. Compared with GeCH₃ film, the band gap of AsCH₃ is enhanced by $\sim$80 meV than that in the case of strained GeCH₃ (108 meV), which is highly useful for experimental observation of QSH effect. In addition, the AsCH₃ and AsOH are intrinsic 2D TIs without applying strain, which are superior to GeCH₃ in the experimental operation. The bulk energy gap in AsOH can reach up to $\sim$0.3 eV, which is the largest one among the arsenene derivatives ever reported.

Compared with pure arsenene, the topological phase transition from trivial to nontrivial phase can attribute to the chemical adsorption effect on the structural and electronic properties of arsenene. As the same group element, some features are very similar to those of antimonene, single Sb(111) bilayer [48]. For example, surface decorated antimonene is 2D TI [39, 46], although pure antimonene is actually a trivial insulator. Previous work [49] has demonstrated that the topological properties in antimonene are related to the Sb–Sb band strength and nontrivial phase can be induced under tensile strain. Given the fact that the chemical groups possess too small SOC strength to induce the topological phase transition, some features of surface decorated antimonene should be analogous to the effect of tensile strain, because the lattice constant of decorated antimonene is indeed larger than that of pristine case. The topological phase transition of arsenene by functionalization can be well understood using the same strategy. The topological properties of functionalized arsenene are closely related to the As–As bond strength, which is well confirmed by the direct comparison with pure arsenene. On the one hand, the effect of surface decoration on arsenene is similar to the effect of in–plane biaxial tensile strain, because the decorated arsenene films have larger lattice constants and smaller buckled heights than pristine arsenene. On the other hand, the surface decoration saturates the dangling bonds of pristine arsenene with the $p_z$ orbitals of As atoms removed, leaving $p_x$ and $p_y$ orbitals around Fermi level.

Strain engineering is a powerful method to tune the electronic and topological properties of 2D materials. A question that is the nontrivial topological nature of surface decorated arsenene stable against strain is now raised.

![Figure 4. Band structures of nanoribbons with armchair edges for (a) AsCH₃ and (b) AsOH films. The gapless edge states (red lines) can be clearly seen. The 1D Brillouin zone is indicated in (a). The Fermi energy is set to zero.](image-url)
In what follows, we will concentrate our mind on the effect of biaxial strain on the topological properties of these three systems including AsCH$_3$ and AsOH films. The biaxial strain is introduced by tuning the in-plane lattice constant, and then the atomic positions are optimized again. The biaxial strain is defined as $\tau = \frac{a - a_0}{a_0}$, where $a_0$ and $a$ denotes the lattice constants of 2D systems without and with strain, respectively. The evolutions of band gap as a function of biaxial strain for AsCH$_3$ and AsOH are plotted in figures 5(a) and (d), respectively. We find that the tensile strain can reach up to at least 8% without band gap closing for both AsCH$_3$ and AsOH films. The global band gaps of AsCH$_3$ films disappear with the compressive strain beyond 6%, whereas the compressive strain tolerance of nontrivial phase of AsOH film can reach 8% and even larger. Within our calculated strain range, the nontrivial topological nature is maintained in these three systems, suggesting their robustness against biaxial strain. Such robust topology makes them potential for experimental realization and applications. To get a better understanding of the strain effect on band structure, the band structures of these two systems under typical strain are presented in figure 5. We find that the bulk band gap of two systems always maintains direct gap under tensile strain, whereas the direct gap becomes indirect with the compressive strain increased, indicating the interatomic coupling can modulate the electronic and topological properties of these systems. In addition, the values of bulk band gaps within calculated strain range are still relatively large, especially for AsOH film. Thus, strain engineering is an effective route to change topological phase by tuning nontrivial band gap of 2D materials.

Conclusions

In summary, the electronic and topological behaviors of arsenene and its derivatives are investigated by first-principles calculations. The topological phase transition from trivial to nontrivial phase can be induced by surface decoration with methyl and hydroxyl groups. The topologically nontrivial phase is predicted in derivative arsenene (AsCH$_3$ and AsOH films). The nontrivial band gaps in these systems are 0.184 eV and 0.304 eV, respectively, so that the QSH effect can be measured experimentally at room temperature. Moreover, we find that although the band gaps in these systems can be decreased by biaxial strain, the nontrivial topological properties are maintained within the strain range of ±6% for AsCH$_3$, and ±8% for AsOH, respectively. It means that their nontrivial topology is robust against external strain. All of these results render that trivial arsenene and nontrivial derivative arsenene are of promising applications in future electronic devices.

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