Robust large-gap topological insulator phase in transition-metal chalcogenide ZrTe₄Se

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Abstract

Based on density functional theory, we investigate the electronic properties of bulk and single-layer ZrTe₄Se. The band structure of bulk ZrTe₄Se can produce a semimetal-to-topological insulator (TI) phase transition under uniaxial strain. The maximum global band gap is 0.189 eV at the 7% tensile strain. Meanwhile, the \( \mathbb{Z}_2 \) invariants (0; 110) demonstrate conclusively it is a weak topological insulator. The two Dirac cones for the (001) surface further confirm the nontrivial topological nature. The single-layer ZrTe₄Se is a quantum spin Hall insulator with a band gap 86.4 meV and \( \mathbb{Z}_2 = 1 \), the nontrivial metallic edge states further confirm the nontrivial topological nature. The maximum global band gap is 0.211 eV at 8% uniaxial tensile strain along the [100] direction. When the compressive strain is more than 1%, the band structure of single-layer ZrTe₄Se produces a TI-to-semimetal transition. These theoretical analysis may provide a method for searching large band gap TIs and platform for topological nanoelectronic device applications.

1. Introduction

Topological insulator (TI) is a new quantum state with gapped bulk band and gapless edge state, and the low-energy scattering of the edge states leads to dissipationless transport edge channels. The two dimension (2D) TI also called the quantum spin Hall (QSH) insulator was first theoretically predicted in 2006, experimentally observed in HgTe/CdTe quantum wells [1, 2] and then was predicted in silicene [3], germanene [4]. The three dimension (3D) TI was first predicted and observed in the Bi₁−ₓSbₓ alloy [5, 6]. These pioneering works opened up the exciting field of TIs, expanding at a rapid pace. In the past decade, the more and more compounds have been predicted to be TIs [7–15], which has undoubtedly a dramatic impact on the condensed matter physics. Recently, the researchers develop codes to compute all characters of all symmetries of stoichiometric materials and find more than 3000 TIs [16, 17]. However, the extremely small bulk band gaps hinder their applications due to weak spin–orbit coupling (SOC). Therefore, the researchers have strong motivation for exploring new TIs or transforming materials into TIs with large band gaps.

Nowadays, the ZrTe₅ has attracted broad attention because of their topological properties [18–24]. The 3D crystal is located near the phase boundary between strong and weak TIs, the 2D is predicted to be a QSH insulator [18]. Later studies indicate that the topological nature in this bulk material is very sensitive to the crystal lattice constants and detailed composition [25, 26]. Last year, the bulk ZrTe₅ was identified as a strong TI at low temperatures by using magneto-infrared spectroscopy [27]. However, there hasn’t yet been a consensus on the bulk topological phase of ZrTe₅ from experiments, especially with several recent contradicting temperature-dependent studies [28–31]. In addition, homologue substitution provides a useful guess for a novel material [32]. Here we modulate electronic structure by using selenium element substitution, which may change the topological properties of ZrTe₅. In order to design a large-gap band...
topological nontrivial phase, one widely used approach is applying strain, which has been proved to be able to regulate the topological properties, such as SiGe [33], TlSbH2 [34], Bi4Br3 [35] and HgSe [36], so we try to use strain to increase the band gap of ZrTe4Se.

In this paper, the first-principles calculations are used to investigate the electronic properties of the ZrTe4Se. We find the band structure of bulk ZrTe4Se can produce a semimetal-to-TI phase transition under certain uniaxial strain. Analyzing of topological properties of bulk ZrTe4Se under the 3% and 8% tensile strain, they are all weak topological insulators (WTIs) with \( Z_2 = (0; 110) \). The single-layer ZrTe4Se is a QSH insulator with \( Z_2 = 1 \), the edge states further confirm the nontrivial topological nature of this material. In addition, we discuss effect of strain on electronic properties of single-layer ZrTe4Se and find the QSH states survives at a large range of strain. When the compressive strain is more than 1%, the band structure of single-layer ZrTe4Se can produce a TI-to-semimetal transition.

2. Computational details

To study the structural and electronic properties of ZrTe4Se, all calculations are carried out using the Vienna *ab initio* simulation package (VASP) [37, 38]. We use the generalized gradient approximation (GGA) [39] for the exchange and correlation potential in the Perdew–Burke–Ernzerhof [40] form. The vacuum region is set to at least 20 Å along \( b \)-direction. The energy cutoff of the plane wave is set to 500 eV with the energy precision of \( 10^{-6} \) eV. The atoms are relaxed until the force per atom falls below 0.01 eV Å\(^{-1} \). A \( 11 \times 11 \times 4 \) \((11 \times 1 \times 4)\) \( \Gamma \)-centered Monkhorst–Pack grid [41] for the bulk materials (2D materials) is used to sample the Brillouin zone (BZ). The theoretical ground states of ZrTe4Se is obtained by fully optimization of the atom positions and lattice constants, then we vary the lattice constants and optimize the atom positions to study the possible topological transition in ZrTe4Se, but the crystal structure symmetry remains the same. To obtain good theoretical lattice constants, the van der Waals (vdw) corrected optB86b-vdw functionals [42, 43] are considered for the bulk materials. To analyze topological properties, the maximally localized Wannier functions (MLWFs) [44] of ZrTe4Se are constructed based on the Zr’s 4d, Se’s 4p and Te’s 5p orbitals by using the Wannier90 code [45]. After successful constructions of the MLWFs, the WannierTools [46] is used to evaluate topological invariants, surface states and edge states.

3. Results and discussion

The ZrTe4Se has the orthorhombic layered structure with \( Cmcm \) (No. 63) space group symmetry, as shown in figure 1(a). The trigonal prismatic chains \( \text{Te}_1-\text{Se}-\text{Te}_1 \) oriented along the \( a \) axis, and these prismatic chains are linked via parallel zigzag chains of \( \text{Te}_2 \) atoms along the \( c \) axis to form a 2D sheet of ZrTe4Se in the \( a-c \) plane. The sheets stack along the \( b \) axis, forming a layered structure. The structural parameters and BZ of ZrTe4Se are presented in table 1 and figure 1(b), respectively. The optimized lattice constants of bulk ZrTe4Se are \( a = 3.9179 \) Å, \( b = 14.3565 \) Å, \( c = 13.6428 \) Å, which are smaller than ZrTe5’s [25]. The binding energy of \(-1.70 \) eV atom\(^{-1} \) indicates the material is stable. The formation energy of 0.09 eV atom\(^{-1} \) indicates the single-layer of ZrTe4Se may be produced by mechanical exfoliation method [47]. Figures 1(c)–(e) show the crystal structure and BZ of the single-layer ZrTe4Se. The relaxed lattice constants are 3.9601 Å and 13.7411 Å, the bond lengths are also slightly different from bulk materials, which can be attributed to the interlayer interactions. We use the electron localization function (ELF) to describe and visualize chemical bonds in solids [48]. The ELF indicates that the probability of existence of a pair of electrons at a some position. The ELF value ranges between 0 and 1, which represents no to complete localization. We have plotted the ELF with an isosurface of 0.5–0.9, see supplemental material (SM) (https://stacks.iop.org/NJP/23/093046/mmedia) figure S1 and figure 2(a). The ELF value is around 0.5 near Zr atoms and 0.9 near Se (Te) atoms, which means that electrons are more localized towards Se and Te atoms. The type of electron localization indicates the ionic type of bonding between Zr and Te (Se) atoms. Moreover, the Te–Te bonding exhibit anti-bonding character rather than bonding character, because the electrons are more localized outside the Te–Te bond. To qualitatively analyze the charge transfer of Zr–Te (or Zr–Se) bond, difference charge density map is plotted in figure 2(b), the white/blue region represents charge accumulation/depletion, respectively. The difference pattern indicates the major charge transfer is from Zr atom to Te (or Se) atom.

In addition, we perform *ab initio* molecular dynamics simulation with a supercell at 300 K to examine thermal dynamic stability of ZrTe4Se. After heating at 300 K for 8 ps with a time step of 2 fs, it is found that the mean value of total potential energy maintains invariable at whole simulation time, see SM figure S2. Neither structure reconstruction nor disruption occur in these materials in figures S3 and S4. These results clearly indicate the materials remain thermally stable at room temperature. Moreover, we
Figure 1. The crystal structure and BZ of ZrTe$_4$Se. (a) The crystal structure of bulk ZrTe$_4$Se. The crystal structure of (c) side and (d) top view single-layer ZrTe$_4$Se, the vacuum stack along the $b$ direction. The BZ of (b) bulk and (e) single-layer ZrTe$_4$Se.

Table 1. The lattice constants $a$, $b$, $c$ (Å) and bond lengths (Å) of ZrTe$_4$Se.

| Material   | $a$   | $b$   | $c$   | $d_{Zr-Te_1}$ | $d_{Zr-Te_2}$ | $d_{Zr-Se}$ |
|------------|-------|-------|-------|---------------|---------------|-------------|
| 2D-ZrTe$_4$Se | 3.9601 | —     | 13.7411 | 2.98          | 2.99          | 2.79        |
| 3D-ZrTe$_4$Se | 3.9179 | 14.3565 | 13.6428 | 2.96          | 2.96          | 2.79        |

Figure 2. ELF and difference charge density of single-layer ZrTe$_4$Se. (a) Structure plot of ELF. Isosurface corresponding to ELF value of 0.8. (b) Difference charge density (crystal density minus superposition of isolated atomic densities). The white (blue) isosurface plots correspond to the charge density accumulation (depletion). Isosurface corresponding to difference charge density of $\pm 0.0095$ eV Å$^{-3}$.

Table 2. Elastic constants (GPa) of bulk ZrTe$_4$Se and ZrTe$_5$.

| Material   | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{22}$ | $C_{23}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ |
|------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 3D-ZrTe$_5$ | 77.20    | 4.77     | 22.19    | 28.85    | 4.20     | 70.74    | 4.92     | 0.66     | 30.93    |
| 3D-ZrTe$_4$Se | 90.12   | 2.92     | 21.59    | 28.20    | 9.30     | 67.07    | 1.27     | 24.43    | 1.43     |

study mechanical stability by calculating elastic constants of bulk materials. For the orthorhombic crystals, there are nine independent elastic stiffness constants in table 2. They fulfill the Born criteria of stability [49], $C_{11} > 0$, $C_{11}C_{22} > C_{12}^2$, $C_{11}C_{22}C_{33} + 2C_{22}C_{13}C_{23} - C_{11}C_{33} + C_{22}C_{13} - C_{33}C_{12} > 0$, $C_{44} > 0$, $C_{55} > 0$ and $C_{66} > 0$, indicating bulk ZrTe$_5$ and ZrTe$_4$Se are all mechanically stable.
Figure 3. The band structures of (a) bulk and (b) single-layer of ZrTe$_4$Se. The red and blue lines correspond to band structures without and with SOC, respectively. The Fermi energy is set to 0 eV.

Figure 4. The variation of band gap as a function of uniaxial strain along the (a) [100], (b) [111] direction of bulk ZrTe$_4$Se and (c) [100] direction of single-layer ZrTe$_4$Se. $E_g$ and $E_{\Gamma}$ represent the globe band gap and direct band gap at the $\Gamma$ point, respectively. The nontrivial $Z_2$ topology survives as long as the globe band gap remains positive.

The calculated band structures for bulk ZrTe$_4$Se are shown in figure 3(a). Without SOC, the band structure presents a semimetal. With the consideration of SOC, the crossing point on the $\Gamma$–Z direction is separated and the conduction band minimum rises, but it has still a semimetal phase. We study the effect of different strain on electronic and topological properties in the bulk ZrTe$_4$Se and find the uniaxial strain along the [010] and [001] directions is little effect on the electronic properties, so the main research tasks focus on the uniaxial strain along the [100] and [111] directions. The variation of band gap ($E_{\Gamma}$ and $E_g$) as a function of uniaxial strain along the [100] direction is presented figure 4(a). $E_g$ and $E_{\Gamma}$ represent the globe band gap and direct band gap at the $\Gamma$ point, respectively. It can be seen that when the tensile strain is more than 1%, the phase transition from a semimetal to semiconductor occurs. The $E_{\Gamma}$ increases monotonically under strain from 1% to 10%, reaching a maximum value of 0.336 eV at 10% and minimum value of 3.1 meV at 1%. The $E_g$ increases first then decreases under tensile strain increases continuously, reaching a maximum value of 0.189 eV at 7%.

The topological properties of ZrTe$_4$Se have been checked and nontrivial topological phases exists from 1% to 10% strain range. We choose ZrTe$_4$Se under [100] strain at 3% as a typical example, the four $Z_2$ invariants are (0; 110) and it is a WTI according to method proposed by Fu, Kane and Mele [50]. The existence of gapless surface states is an additional commonly employed criterion for TI. The band structure and (001) surface state are shown in figure 5. The VBM and CBM are separated resulting 0.103 eV band gap. In the exotic topological surface state, two Dirac cones located at the $T$ and $K$ points respectively for the (001) surface. Then we study the effect of uniaxial strain along the [111] direction, the variation of band gap as a function of strain is presented figure 4(b). The $E_{\Gamma}$ increases monotonically under strain from 1% to 9%, the $E_g$ increases with strain and reaches a maximum value of 91.6 meV at 8%. When the strain is more than 2%, a semiconductor phase occurs. In addition, we find it is still a WTI with same $Z_2$ under 2% to 9% uniaxial strain. The band structure and (001) surface state for ZrTe$_4$Se under 8% strain are presented in figures 5(c) and (d), two Dirac cones located at the $R$ and $K$ points confirm it is WTI.

The calculated band structures for a single-layer ZrTe$_4$Se are displayed in figure 3(b). It is a gapless semimetal with the CBM across the Fermi energy without consideration of SOC, the VBM and CBM near the $\Gamma$ point almost touch each other. With consideration of SOC, the band structure produces a
semimetal-to-semiconductor transition with a band gap of 86.4 meV. By presenting the orbitals-resolved band structures in figure 6, it can be seen the bands around the Fermi level are mainly derived from Te\textsuperscript{2}-5p and Se-4p orbitals. It is noticed that GGA results are relatively reasonable in ZrTe\textsubscript{5} system \cite{29, 51–53}, while HSE06 results (see figure S5) will generate a larger band gap and may require a larger strain to make the phase transition occur.

The evolution lines of Wannier centers in figure S6 show it is a nontrivial QSH insulator with $Z_2 = 1$ and the important character of helical edge states also appear, as shown in figure 7. Helical edge states \cite{54, 55} are very useful for electronics and spintronics owing to their robustness against scattering. There is a Dirac cone at the $\Gamma$ for the $a$ axis edge. Fermi velocity of helical edge states, which is an important quantity related to applications, is about $3.2 \times 10^5$ m s$^{-1}$, comparable to $10^6$ m s$^{-1}$ in graphene \cite{56}. For
the $c$ axis edge, the symmetric edge structure leads to two Dirac cones located at opposite $\Gamma$ points. The nontrivial metallic edge states further confirm the nontrivial topological nature of the monolayer ZrTe$_4$Se.

To get a physical understanding of the topological nature, we start from atomic orbitals and consider the effect of chemical bonding on the energy levels at the $\Gamma$ point for monolayer ZrTe$_4$Se. For the convenience of discussion, we define coordinate system with $x$, $y$ along $a$, $c$ axes, respectively. The origin of the coordinate system located on Zr site, so the inversion center located at (0.25, 0.25). We note single-layer ZrTe$_4$Se has space group $Pmmn$ ($D_{12}^h$), which is nonsymmorphic, the $Z_2$ index of the material is fully determined by the energy order of the bands at the $\Gamma$ point [18]. From the orbitals-resolved band structures, we find the band inversion happens between the Te$_2$-p$_x$ and Se-p$_y$, as shown in figure 8. For (I) process, there are four equivalent Te$_2$ atoms; they are fourfold degenerate. There are two equivalent Se atoms, they are double degenerate. For (II) process, the strong intrachain covalent bonding will split them into bonding and antibonding states. The Te$_2$ and Se have inversion symmetry and can be divided into two classes with $p = +1$ or $p = -1$. For (III) process, the weak interchain coupling will further change the Se’s states and split Te$_2$ states to single non-degenerate states. As a result, only the Te$_2$ state has odd parity, which leads to the QSH state. The band gap is opened by SOC effect, but SOC effect has nothing to do with topological properties.

Further more, we study electronic properties of single-layer ZrTe$_4$Se under different strain to explore the possible phase transition. For the uniaxial strain along the [100] direction, the variation of band gap as a function of strain is presented figure 4(c). The $E_F$ increases monotonically under strain from $-6\%$ to 10%. The $E_g$ increases under tensile strain increases continuously and reaches a maximum value of 0.211 eV at 8% tensile strain. It can be seen that the nontrivial topological phases exists over a wide strain from $-1\%$ to 10%, such robust topology against lattice deformation makes it easier for experimental realization and characterization on different substrate. When the compressive strain is more than 1%, the band structure produces a TI-to-semimetal transition.
4. Conclusion

In summary, the bulk and single-layer ZrTe₄Se is mechanically and dynamically stable, so it is possibly to be prepared. The bulk ZrTe₄Se is predicted a new 3D WTI with $Z_2$ invariants $(0; 110)$ under a large range of uniaxial strain. When the tensile strain along the $[100]$ ($[111]$) direction is more than $1\%$ ($2\%$), the band structure of bulk ZrTe₄Se produces a semimetal-to-TI transition. The maximum global band gap is $0.189$ eV at the $7\%$ tensile strain along the $[100]$ direction. The two Dirac cones for the $(001)$ surface confirm the nontrivial topological nature at the $[100]$ ($[111]$) tensile strain $3\%$ ($8\%$). These calculations demonstrate the bulk ZrTe₄Se can be turned into a 3D TI via proper strain engineering. The single-layer ZrTe₄Se is a QSH insulator with a band gap $86.4$ meV and $Z_2 = 1$, the edge states further confirm the nontrivial topological nature of this material. The Dirac point located at the band gap has a high velocity about $3.2 \times 10^5$ m s$^{-1}$. The QSH state survives at a large range of strain from $-1\%$ to $10\%$, indicating its robust stability against the strain. The maximum global band gap is $0.211$ eV at $8\%$ uniaxial tensile strain along the $[100]$ direction. When the compressive strain is more than $1\%$, the band structure of single-layer ZrTe₄Se produces a TI-to-semimetal transition. These findings make the ZrTe₄Se is an excellent candidate for large-gap TI and may provide a platform for realizing low-dissipation quantum spintronic devices.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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