Predicting a Novel Phase of 2D SiTe$_2$

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**ABSTRACT:** Layered IV$^-$VI$_2$ compounds often exist in a CdI$_2$ structure. Using the evolution algorithm and first-principles calculations, we predict a novel layered structure of silicon ditelluride (SiTe$_2$) that is more stable than the CdI$_2$ phase. The structure has a triclinic unit cell in its bulk form. The atomic arrangement indicates the competition between the Si atoms’ tendency to form tetrahedral bonds and the Te atoms’ tendency to form hexagonal close-packing. The electronic and vibrational properties of the predicted phase are investigated. The effective mass of an electron is small among two-dimensional (2D) semiconductors, which is beneficial for applications such as field-effect transistors. The vibrational Raman and IR spectra are calculated to facilitate future experimental investigations.

**1. INTRODUCTION**

The investigation and characterization of two-dimensional (2D) materials have been increased significantly since the last decade. Synthesis of many novel 2D materials including graphene,$^{1,2}$ hexagonal boron nitrides,$^{3,4}$ transition metal dichalcogenides,$^{5,6}$ phosphorene,$^{7,8}$ and silicene$^{9,10}$ drives rapid progress in the field. These materials attract significant interest because of their intriguing properties different than in their bulk forms due to the reduced dimension, such as quantum confinement, mechanical flexibility, lack of dielectric screening, and large surface areas. These properties are beneficial for a wide range of potential applications in optoelectronics,$^{11,12}$ chemical sensors,$^{13}$ photovoltaics,$^{14}$ energy storage,$^{15}$ nanoelectronics,$^{16}$ and many more.

The IV$^-$VI$_2$ compound family contains a number of materials with layered crystal structures from which 2D crystalline mono- and multilayers can be obtained. The IV$^-$VI$_2$ group includes 2D SnSe$_2$, SnS, GeS, and GeSe$_2$ which adopt a puckered layer structure with C$_{2v}$ symmetry. The 2D IV$^-$VI$_2$ materials include SnSe$_2$ and SnSe$_2$, whose bulk forms adopt the CdI$_2$-type crystal structures with a P3m1 space group. The Si$_x$-Te$_y$ system is a particularly interesting member of the IV$^-$VI$_2$ family, as Si is a small group 4 element, and Te is a large group 6 element. The silicon telluride (Si$_2$Te$_3$)$^{21,22}$ is the most studied Si$_x$-Te$_y$ compound. It is the only known IV$^-$VI$_2$ material with a layered structure$^{21,30}$ and features a unique structural variability because of the orientation of silicon dimers.$^{24}$ The other Si$_x$-Te$_y$ compound is silicon ditelluride (SiTe$_2$)$^{31-34}$ whose electrical, thermal, and magnetic properties have recently drawn a number of investigations.$^{35-37}$ The crystal structure of SiTe$_2$ is identified to be the CdI$_2$-type$^{34,38}$ as other 2D IV$^-$VI$_2$ materials, although it was suggested that it might also exist in the Si$_2$Te$_3$ structure with Si deficiency.$^{39}$

In this paper, we use results from the evolutionary algorithm and first-principles calculations to predict a new layered crystal structure of SiTe$_2$ that is more stable than the CdI$_2$-type structure. The predicted bulk structure has a triclinic unit cell. The atomic structure indicates the competition between the Si atoms’ tendency to form tetrahedral bonds and the Te atoms’ tendency to form hexagonal close-packing. The material has a low electron effective mass and anisotropic hole effective mass that can be beneficial for potential applications. The Raman and IR spectra are calculated, which can be useful for future experimental investigations.

**2. RESULTS AND DISCUSSION**

2.1. Structures. A total of 382 stable crystalline structures are generated by the evolution algorithm. In Figure 1a, we plotted the energy per atom of each of the generated structures. We obtain the lowest energy structure with the total energy of $-3.88$ eV/atom. The top and side views of the corresponding structure are shown in Figure 2a,b. The structure features a triclinic crystal lattice with a space group P1. The primitive unit cell consists of three atoms (one Si atom and two Te atoms). The Wyckoff sites are Si (0, 0, 0), Te ($-0.0383, 0.4632, 0.2330$), and Te (0.5360, 0.0391, $-0.2330$). The lattice parameters of this lowest energy of SiTe$_2$ are shown in Table 1. The evolutionary algorithm search also found the CdI$_2$-type structure of SiTe$_2$ that was previously reported$^{34,38}$ with the total energy of $-3.81$ eV/atom. Thus, the new

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predicted structure is energetically more stable than the common CdI₂-type structure that has been reported in SiTe₂.

It is interesting to discuss why this structure exists in SiTe₂ and is more stable than the CdI₂-type structure. In Figure 2c, we show the local bonding structure of Si in this new structure. The Si atom is clearly tetrahedrally bonded, which indicates covalent bonding from sp³ hybridization of Si 3s and 3p orbitals. Meanwhile, in the CdI₂-type structure, the cations are six-coordinated (Figure 2d). Given the strong tendency of Si to form such covalent bonds, it is reasonable to state that forming six-coordinated Si is associated with an energy penalty compared with four-coordinated Si. On the other hand, the tetrahedral around the Si atoms are strongly distorted. As shown in Table 2, there is a large variety of the Te–Te distances in the tetrahedral surrounding the Si atom, ranging from 3.945 to 4.516 Å. The reason for this distortion is that due to its large size, the Te atom prefers the hexagonal close-packed (HCP) structure, which is not fully compatible with the tetrahedral bonding of Si. The competing requirements lead to the distorted bonding around Si atoms along with a slightly distorted HCP packing of Te, as can be seen in Figure 2ef.

As the new structure forms because of strong sp³ hybridization from atoms in the group 4 (thus a small atomic number) and large size of atoms in the group 6 (large atomic number), it may also show up in other IV–VI₂ materials as the ground state. One possible candidate would be CSe₂. However, although C atoms can form strong covalent bonds through sp³ hybridization, they can also easily adapt sp² hybridization that enables other bonding configurations. Because of the sp³ hybridization of carbon, CSe₂ is known to exist in a linear molecular geometry Se≡C≡Se instead of the six-coordinated CdI₂ structure. It would be interesting to investigate how the new structure competes with the linear molecular form of CSe₂ at various pressures.

2.2. Dynamical Stability. To determine whether the predicted structure is dynamically stable, we calculated the phonon dispersion of bulk SiTe₂ along the high symmetry lines of Brillouin zones using the finite displacement method. The phonon spectrum (Figure 3a) shows no significant negative frequencies, therefore indicating that the structure is dynamically stable. The very small negative frequencies in the acoustic mode near the Γ point are numerical artifacts due to the use of a finite fast Fourier transform (FFT) grid. The dynamical stability is further examined by the ab-initio molecular dynamic (AIMD) simulation at 500 K. As shown in Figure 3b, the total energy fluctuates during the simulation without any sudden drop of the energy that would indicate a phase transition. The snapshot confirms that the structure remains stable during the AIMD simulations.

Figure 4 shows the total energy per fu as a function of interlayer separation d. Comparing the total energy at the minimal (d = 3.853 Å) with the energy at large separation (d = 13.793 Å), we obtain a coupling energy of 21 meV/fu The
small value of the coupling energy suggests that the monolayer can be experimentally synthesized. Figure 5a shows the phonon dispersion of the monolayer SiTe₂, which also shows no significant negative frequencies, indicating that the monolayer is dynamically stable. AIMD simulation at 500 K further confirms the dynamical stability, as shown in Figure 5b.

2.3. Electronic Structure. To understand the electronic properties of SiTe₂, we studied the band structures of both the bulk and monolayer along the high symmetry lines of Brillouin zones using the density functional theory (DFT) method. Figure 6a,b represents the electronic band structures of bulk and monolayer SiTe₂, taking into account the spin–orbit interaction. The band gap is 0.206 eV for bulk and 0.552 eV for the monolayer. When excluding the spin–orbit interaction, the band gap increases by 0.170 eV in bulk and 0.178 eV in the monolayer. Since DFT is known to underestimate the band gap, we used the hybrid DFT method with the HSE06 functional. Figure 7 below represents the band structures of SiTe₂ under the HSE06 approach. The band structures are similar to the DFT band, except that the band gaps for bulk and monolayer have increased to 0.831 and 1.222 eV, respectively. When excluding the spin–orbit interaction, the band gap increases by 0.186 eV in bulk and 0.180 eV in the monolayer at an HSE level.

The effective masses of the electrons and holes in SiTe₂ are obtained by fitting the DFT bands near the CBM and VBM using the relationship \( m^* = \frac{\hbar^2}{2E} \left( \frac{2\pi^2}{m} \right) \). The results are shown in Table 3. The electron effective mass bulk is 0.116\( m_0 \), which is comparable to black phosphorous (\( m^* = 0.12m_0 \))⁴¹ and 4 times smaller than MoS₂ (\( m^* = 0.45m_0 \)).⁴² The low electron effective mass suggests high electron mobility, which is beneficial for applications such as field-effect transistors. An in-plane anisotropy is observed for the holes, where the effective mass along the \( y \)-direction is 3–4 times the value along the \( x \)-direction. Such anisotropy may be beneficial for designing devices such as angle-dependent optoelectronic applications.⁴³ It should be clarified that the \( x \)- and \( y \)-directions (shown in Figure 2a) are not the same as the directions toward \( X \) and \( Y \) points, as shown in Figures 6 and 7. The \( X \) and \( Y \) points are along the reciprocal lattice vectors corresponding to the vectors \( a \) and \( b \) shown in Figure 2a. The names of \( X \) and \( Y \) points come from the standard notation of the first Brillouin zone of a triclinic crystal lattice.⁴⁴ Figure 8a shows the partial and total densities of states (DOS) of bulk SiTe₂, from HSE calculations. The conduction bands consist both of the \( p \) orbitals of Si atoms and the \( p \) orbitals of Te atoms. Meanwhile, the valence bands are mainly due to the \( d \) orbit of Te atoms. To better understand the

| Table 1. Structural Parameters of Predicted Bulk and Monolayer SiTe₂ |
|-------------------------------|----------------|----------------|----------------|----------------|----------------|
|                             | \( a \) (Å)   | \( b \) (Å)   | \( c \) (Å)   | \( \alpha \) (deg) | \( \beta \) (deg) | \( \gamma \) (deg) | \( d_{0−\gamma} \) (Å) |
| bulk                        | 3.945         | 3.945         | 7.076         | 83.68           | 83.77           | 75.98           | 2.561 |
| monolayer                   | 3.941         | 3.941         | N/A           | N/A             | N/A             | N/A             | 2.558 |

| Table 2. Nearest Neighbor Te–Te Distances in Bulk SiTe₂ |
|-----------------|----------------|----------------|
| \( d_{1−2} \) (Å) | 3.945          | 4.070          |
| \( d_{2−3} \) (Å) | 4.516          | 4.502          |
| \( d_{3−4} \) (Å) | 4.070          | 3.945          |

Figure 3. (a) Phonon band structures of bulk SiTe₂. (b) Snapshot of AIMD simulation at 500 K and the variation of total energy in AIMD simulation during a timescale of 20 ps.

Figure 4. Total energy per fu as a function of interlayer separation \( d \).
contribution of each atomic orbitals to the band structures, we analyze the wave functions at band edges. Figure 8b,c represents the square of the wave functions at CBM and VBM. It can clearly be seen that the s orbitals of Si atoms along with p_x + p_y orbitals of Te atoms play a major role at CBM, while the VBM mainly consists of p_x + p_y orbitals of Te atoms.

It is interesting to note that the p_x + p_y orbitals from adjacent Te atoms tend to align with the Te–Te direction, which indicates the σ-type bonding between Te atoms.

2.4. Bonding Analysis. To explore the chemical bonding of SiTe_2, we calculate the electron localization function (ELF) in bulk SiTe_2. The results are shown in Figure 9. We clearly observe the lone pairs on the Te atoms and the Si–Te bonds that are localized between the Si and Te atoms. We also performed the Bader charge analysis for bulk SiTe_2 from which we found a net electron transfer of 0.71e from each Si atom to two Te atoms. The transferred charge is equally divided between the two Te atoms. This charge transfer is consistent with the ELF results.
with the fact that that a Si atom is less electronegative than a Te atom.

2.5. Raman and IR Spectra. Vibrational spectroscopy is widely used to characterize 2D materials. To facilitate future experimental investigation of the predicted phase of SiTe$_2$, we present the calculated Raman spectra of bulk and monolayer SiTe$_2$ with the respective vibrational modes in Figure 10. We found that the bulk SiTe$_2$ has three major Raman peaks at 144.06, 261.73, and 409.90 cm$^{-1}$, whereas the monolayer SiTe$_2$ has two major Raman peaks at 147.35 and 413.88 cm$^{-1}$. The 144.06/147.35 cm$^{-1}$ peak corresponds to the out-of-plane vibration mode of the Te atoms, while the 409.90/413.88 cm$^{-1}$ peak corresponds to the out-of-plane vibration mode of the Si atoms. The peak at 261.73 cm$^{-1}$ in bulk SiTe$_2$ corresponds to the in-plane vibration of Si atoms. This mode has negligible Raman intensity in the monolayers while being significant in bulk, indicating the effect of interlayer coupling.

Figure 11 shows the calculated IR spectra. The bulk SiTe$_2$ has two major peaks at 269.89 and 409.00 cm$^{-1}$. The former corresponds to an in-plane vibration mode of Si atoms that is orthogonal to the Raman-active in-plane Si vibration mode at 261.73 cm$^{-1}$, while the latter is the same as the Raman-active out-of-plane Si vibration mode. The monolayer SiTe$_2$ has only one major Raman peak at 271.79 cm$^{-1}$. The mode around 410 cm$^{-1}$, which is IR active in bulk, is inactive in the monolayers, again indicating the effect of interlayer coupling. This feature may be useful for identifying the thickness of the SiTe$_2$ layers in experiments.

3. SUMMARY

In summary, we use the evolution algorithm coupled with the first-principles calculations to predict a novel 2D layered structure of silicon telluride (SiTe$_2$), which is different from the known layered CdI$_2$-type structure in IV–VI$_2$ materials. The structure features a distorted tetrahedral bonding for Si atoms and a distorted hexagonal close-packing of Te atoms,
indicating that structure forms as a compromise of these two competing requirements. We confirm the dynamical stability of the structure using both phonon dispersion and the AIMD simulations. Electronic properties are investigated by both the DFT and hybrid DFT methods. The new SiTe2 phase is a semiconductor with an indirect band gap in its bulk form and a direct band gap in its monolayer form. It features electron effective mass of 0.12m0, which is low among 2D semiconductors. The Raman and IR spectra for the bulk and monolayers are also predicted.

4. COMPUTATIONAL METHODS

4.1. Evolutionary Algorithm. The global search of stable crystal structures of bulk SiTe2 is done using the evolutionary algorithm as implemented in the universal crystal structure predictor (USPEX).45,46 The USPEX code has been shown to produce similar results as other structure prediction code such as crystal structure analysis by particle swarm optimization (CALYPSO).45,46 The initial population (first generation) consists of 30 structures generated randomly using the space group symmetry under fixed chemical composition Si/Te = 1:2. The number of structures in each generation is kept constant. The genetic evolutionary could stop if the best structure did not change for ten generations. We use 60% of the current generation to produce the next generation. In total, 50% of the generation was produced by heredity, 30% of the generation was produced randomly from space groups, and 20% of the generation was produced by soft mutations in each generation afterward. A three-atom cell of SiTe2 is included in the structure search algorithm. The external pressure is set to zero. The structural relaxations and total energy calculations are carried using the density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) code.47 The pseudopotentials are constructed under generalized gradient approximation (GGA). The global break conditions for the electronic and ionic steps are 10−5 eV and 10−2 eV/Å, respectively. During the evolutionary search of structures, the maximum kinetic energy cutoff for the plane-wave basis is 320 eV.

4.2. Density Functional Theory Calculations. After we found the most stable structure of bulk SiTe2, we construct the monolayer and investigate the electronic properties of both bulk and the monolayer through DFT and hybrid DFT calculations. These calculations are carried out using the VASP code and the same pseudopotentials as in the evolutionary algorithm search. We use the PBE functional for DFT calculations and hybrid HSE06 functional50,51 for hybrid DFT calculations. The convergence conditions for the electronic and ionic steps are 10−9 and 10−8 eV, respectively. After ionic relaxation, the residual force is smaller than 10−4 eV/Å. The kinetic energy cutoff for the plane-wave basis set was 500 eV. Brillouin zones for bulk and monolayer SiTe2, respectively, were sampled at 13 × 13 × 7 and 13 × 13 × 1 k-point grids centered at the Γ point. The spin−orbit coupling effects are considered for the band structure calculations. For the model of the monolayer structure, a vacuum of 13.7 Å is inserted between the periodic replicas of the monolayer to avoid artificial interactions. To confirm the dynamical stability, we performed the phonon calculations of a 5 × 5 × 5 supercell of the bulk and a 5 × 5 × 1 supercell of the monolayer using the finite displacement method as implemented in the Phonopy program.53 To further verify the dynamical stability, we carried out ab-initio molecular dynamic simulations (AIMD) in a 4 × 4 × 2 supercell of the bulk and a 4 × 4 × 1 supercell of the monolayer at 500 K. The time step was set to 2 fs with a total simulation time of 20 ps.

4.3. Raman and IR Spectra. We carried out density functional perturbation theory (DFPT)53 calculations as implemented in the Quantum Espresso package54 to obtain the Raman and IR spectra of bulk and monolayer of SiTe2. The calculations use the Perdew–Zunger functional55 under the local density approximation and the norm-conserving pseudopotential.56 The reciprocal space was sampled with a k-point grid of 13 × 13 × 7 for bulk and 13 × 13 × 1 for a monolayer centered at the Γ point. The cutoff energy of the plane-wave basis is 80 Ry. The Raman and IR spectra calculations start from the charge densities that are converged to 10−14 Ry in total energy.
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